1972-06

# An examination of the cold tip theory of whisker growth.

Hovermale, Mark Daniel

Monterey, California. Naval Postgraduate School

# AN EXAMINATION OF THE COLD TIP THEORY OF WHISKER GROWTH

Mark Daniel Hovermale

# NAVAL POSTGRADUATE SCHOOL
## Monterey, California

# THESIS

AN EXAMINATION OF THE COLD TIP THEORY OF WHISKER GROWTH

by

Mark Daniel Hovermale

Thesis Advisor: William M. Tolles

June 1972



*Approved for public release; distribution unlimited.*

An Examination of the Cold Tip
Theory of Whisker Growth

by

Mark Daniel Hovermale
Ensign, United States Navy
B. S., United States Naval Academy, 1971

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the

NAVAL POSTGRADUATE SCHOOL
June 1972

## ABSTRACT

A new consideration in the growth mechanism of whiskers is examined. The heat flow due to the shape of the crystal and the thermodynamics of the growth reaction is believed to be an important factor in the unidirectional growth observed in whiskers. A computer program was formulated to model the heat flow as well as a method to calculate the time necessary for the temperature changes to occur.

It was found that there is substantial reason to believe the whisker tip is significantly cooler than the sides. This phenomenon is referred to as the cold tip mechanism which provides a preferential growth site for reaction at the tip.

TABLE OF CONTENTS

## LIST OF DRAWINGS

# I. INTRODUCTION

The requirements of today's technology have brought about the demand for more high strength, light-weight materials. In the past few years, fiber reinforced composite materials have shown promise in fulfilling this demand. Of concern in this paper is the growth of a class of fibers called whiskers. The terms "fiber" and "whisker" have been defined by Rauch, Sutton, and McCreight in Ref. 1 as:

> Fiber - Any material in an elongated form such that it has a minimum length to a maximum average transverse dimension of 10:1, a maximum cross-sectional area of $7.9 \times 10^{-5}$ in.$^2$ and a transverse dimension of 0.010 in.
>
> Whisker - Any material that fits the definition of a fiber and is a single crystal.

Whiskers are exceptionally suited to this application due to their high strength. This strength has been shown by Brenner (Ref. 2) to approach the theoretical cohesive strength of solid matter, which lies between three and seventeen per cent of the modulus of elasticity. This remarkable property has been attributed to the crystalline perfection and small dimensions that minimize defects or dislocations which weaken bulk materials. Frank has estimated that a bulk material of comparable size to a whisker would contain $10^8$ dislocations (Ref. 3).

Currently, the major reinforcing whisker in use is of the ceramic type. Metallic whiskers have not been used for engineering purposes to as great an extent due to problems of fabricating them into a matrix.

In general, a metallic whisker undergoes metallurgical reaction with the matrix at high temperature and during fabrication. Dislocations are easily introduced into most metallic whiskers, and, in comparison to ceramic whiskers, possess a low modulus and high density.

To solve the problem of fabrication and production, an understanding of the basic mechanism for metallic whisker growth is necessary. There are two generally accepted mechanisms for whisker growth. The first mechanism proposed is based upon the screw dislocation theory (Ref. 3). Basically, this mechanism postulates a permanent crystal imperfection at the tip of the whisker. The dislocation becomes a preferred growth site for the material which diffuses up the sides of the whisker. The second common theory is that of the vapor-liquid-solid (VLS) mechanism (Ref. 1). Here an impurity becomes a site for condensation of the material from the atmosphere. A liquid droplet forms, becomes supersaturated, and the growth step occurs when the solid precipitates from the liquid.

Several laboratory experiments were also carried out in the course of this investigation concerning growth of whiskers. Growth of iron and copper whiskers was examined since these two metals are used widely for engineering purposes, and the problem under consideration was the separation of defect free whiskers from the substrate. This investigation involved growth of whiskers on granular substrates such as charcoal, while other experiments delt with transport of the reaction vapor from its source to nucleating sites adjacent to the starting materials.

In the course of experimentation it was found that the mechanisms proposed earlier had some shortcomings when used to explain the results. Another process was proposed to explain the observed growth in terms of heat transfer.

The new theory was called the cold tip mechanism. This scheme proposed that the heat flow in the rod shaped whisker made the tip cooler than the sides. The cooler tip provided a position for concentration of the reactant molecules which had migrated to the whisker surface. Consequently, the tip became a preferred growth site. An accompanying phenomenon called thermal runaway was predicted. This term described the effect of an endothermic reaction withdrawing heat from the metal thus cooling the surface at the tip. Consequently, the tip should become an even more preferable growth site.

To examine this hypothesis, a mathematical model of a cold tip whisker was formulated. The finite difference technique was used to solve the differential equations describing conduction and convection. Results of this treatment were used to show the necessary conditions for the cold tip phenomenon to occur.

## II. TRADITIONAL POSTULATED GROWTH MECHANISMS

### A. SCREW DISLOCATION THEORY

#### 1. Steps Leading to its Creation

A theory of crystal growth from the vapor phase was initially developed by Volmer in 1922. His early work gave him the impression that the mechanism involved an adsorbed layer, and from this, the two-dimensional nucleation mechanism was formulated. Essentially this theory postulated growth occuring as follows: first, consider a flat crystal surface in contact with a vapor. Assume that this surface is partially covered by another layer. If the pressure of the vapor is raised by an amount called $\Delta p$ above the equilibrium pressure the layer will grow at a speed proportional to $\Delta p$ until the surface is covered. To start a new layer, a two-dimensional nucleus (critical nucleus) must be formed. The number of critical nuclei created per second is proportional to exp $(-A_0/kT)$, where $A_0$ is the activation energy for nucleation. Burton and Cabrera in Ref. 4 calculated a corrected $A_0$ by:

$$\phi = LkT \ln\alpha \quad A_0 = \phi^2/(kT \ln \alpha)$$

where $\alpha$ is the saturation ratio, defined as the ratio between the actual concentration in the vapor to the equilibrium value, $\phi$ the energy of interaction between nearest neighbors, and $L^2$ the number of molecules in the critical nucleus. Using the above equations,

reasonable values of $A_0$ were calculated to account for self-nucleation of new crystals from the vapor as well as from new liquid drops at saturation ratios of 10 and 5 respectively (Ref. 3). However, 1.5 was calculated to be the lowest $\alpha$ possible to obtain reasonable rates of crystal growth by means of two-dimensional nucleation. This result deviated markedly from observed crystal growth which occurred in environments where supersaturation ratios were of the order of 1.01.

2. Screw Dislocation Mechanism

To account for this discrepency, F. C. Frank (Ref. 3) introduced the screw dislocation mechanism. The screw dislocation was pictured as a spiral staircase with the steps made up of crystals

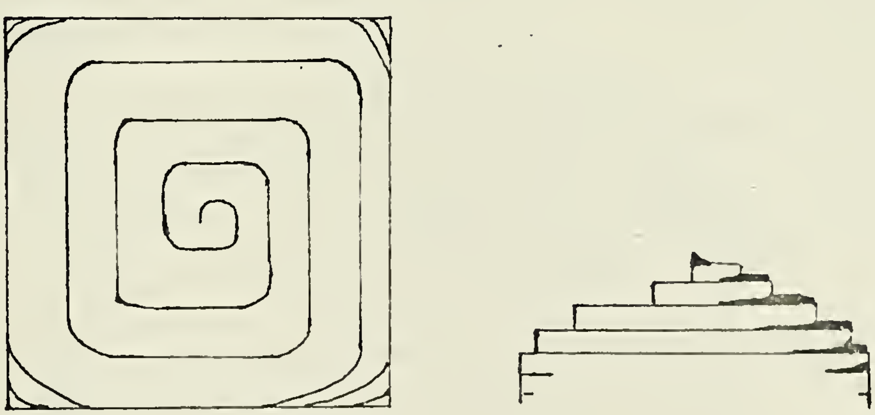


Fig. 1 Screw dislocation surrounded by growth cone.

within the lattice at the tip of the whisker. These indentations formed preferential growth sites. The dislocation was self-perpetuating in that as the steps were filled in by new crystals, and the surface of the new growth was of the same orientation as the original growth site. At the same time, the screw dislocation would justify the one-dimensional growth observed in whiskers. This mechanism has been shown to occur in liquid phase crystallization by the observance of growth spirals of the above configuration on paraffin. However, conclusive experimental evidence that screw dislocations exist in metal whiskers grown from the vapor phase has yet to be found.

## B. VAPOR-LIQUID-SOLID (VLS) MECHANISM

Of the two major whisker mechanisms, VLS has been more recently introduced. First, some of the observations which led to the proposed mechanism for silicon were (Ref. 1):

1. Silicon whiskers were dislocation free.
2. Certain impurities were essential for growth.
3. Whisker growth was a two-stage process consisting of : (a) A fast initial extension in length (leader growth) followed by (b) a slow increase in thickness (layer growth). It was also found that impurity concentration in leader growth was greater than in the layer growth.
4. Rapid initial extension in length occurred by addition of material at the tip.
5. A "liquidlike" globule was often observed at the tip of the whisker.

The initiating step in whisker growth by this mechanism is a "seed" made up of an impurity which has melted. The liquid surface has a higher accomodation coefficient than the side of the whisker and becomes a preferred growth site. The liquid becomes supersaturated

with the deposited material from the vapor, and the material precipitates for the growth step.

Since the process is essentially a condensation reaction, the growth rate J can be estimated from gas kinetics as:

$$J = a\,\sigma\,p_o(2\pi m\,kT)^{-\frac{1}{2}}$$

Where:

a = accomodation coefficient - the fraction of impinging atoms which deposit on the surface.

$\sigma = \frac{(p-p_o)}{p_o}$ - defined as supersaturation where p is the vapor pressure and $p_o$ is the equilibrium vapor pressure of the solid at the temperature T.

m = mass of molecule.

k = Boltzmann's constant.

The accomodation coefficient depends on the perfection of the surface as well as on $\sigma$ . Thus for a "perfect" crystal no spaces for molecules to attach themselves to the whisker exist, and the accomodation coefficient is small. The rougher the surface the higher the coefficient,therefore a liquid can be considered the ideally "rough" surface since it is composed of accomodation sites only interatomic distances apart. Consequently, the VLS mechanism should approach the ideal growth rate even at lower supersaturations.

For VLS to operate, the liquid must be stable, imposing a condition upon the diameter of a VLS whisker. The stability of a droplet of curvature $r$ in its own vapor depends on $\sigma$ by the expression for the

minimum curvature:

$$r\ min = \frac{2(\sigma\ LV)V_L}{RT \ln \sigma}$$

Where:

$\sigma$ LV is the liquid - vapor interfacial energy.

$V_L$ is the liquid molar volume.

R is the gas constant.

Also, the VLS mechanism necessitates having an impurity meeting the following specifications: (1) It must from a liquid solution with the material to be crystallized at the growth temperature. (2) The distribution coefficient defined as $k = C_s / C_l$, where $C_s$ and $C_l$ are the solubilities of the solid and liquid respectively, must be less than one. (3) The equilibrium vapor pressure of the impurity should be small. Evaporation of the impurity lessens the size of the liquid globe, thus decreasing the whisker diameter. (4) The seed must be inert to chemical reaction with the environment. (5) The agent should have the proper wetting characteristics as determined by the interphase energies. (6) For controlled unidirectional growth, the solid-liquid interface must have a well defined crystal structure.

The VLS mechanism has much more substantial evidence than the screw dislocation mechanism. However, there is no proof that this applies to the growth of the pure metallic whiskers.

# III. EXPERIMENTAL

## A. GROWTH OF IRON WHISKERS

The method used for growing iron whiskers was introduced by Brenner (Ref. 5) in 1956. The iron was produced in whisker form from the reduction of its halide by hydrogen at a temperature above the melting point of the salt.

$$FeX_2 + H_2 \rightarrow Fe + 2\,HX$$

Where X = a halide.

The general procedure was as follows: the starting materials were prepared and placed upon a steel liner which was used so that the resultant growth wouldn't be damaged when removed from the boat as well as to keep the boat clean. Liner and boat were placed in the cooling section and the rubber stoppers positioned as shown in Fig. 2 so that the tube was air tight. An inert atmosphere was created by flushing the system with helium at a rate of 1.0 cubic foot per hour (CFH) for ten minutes on the first run. For subsequent runs flushing time was decreased to approximately five minutes due to the smaller amount of oxygen present within the quartz tube. On the initial run of a series care was also taken to flush the tubing leading to the hydrogen tank to remove any air present. After the chamber was flushed, the hydrogen flow was introduced. A short interval of time was allowed to pass before the boat was moved into the hot region of the chamber so as

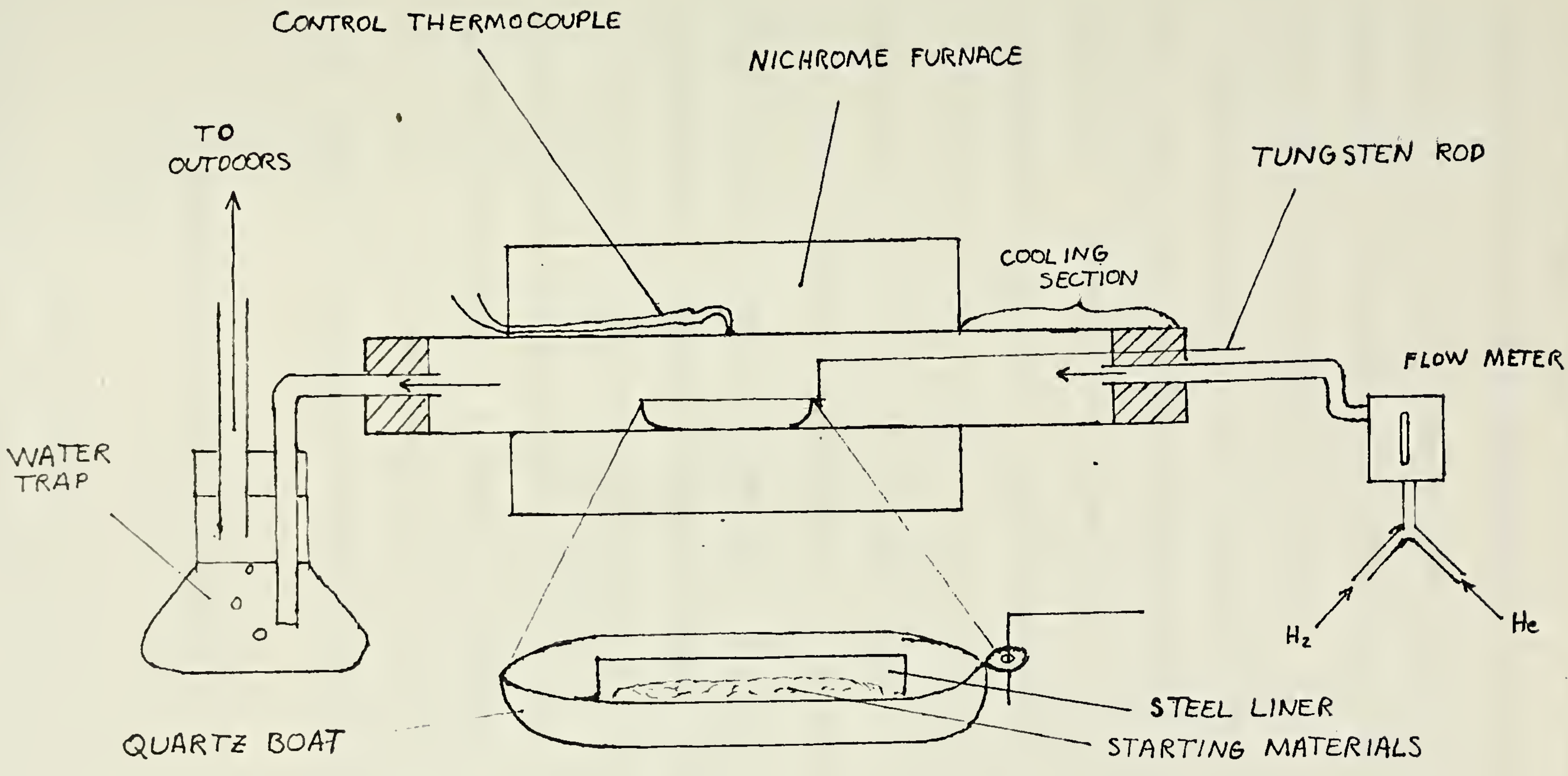



Fig. 2

Apparatus for growth of whiskers.

to have a hydrogen atmosphere present for the initial reaction. When the desired time for the growth had passed the boat was moved into the cooling section, and the system flushed again with helium. The boat was removed, and stopper replaced so as to prevent an excessive amount of air from entering the chamber.

This was the general procedure used for growing whiskers. However, several modifications were made and will be noted in the following experiments. A word about nomenclature in the labeling of experiments is appropriate at this time. The convention used in the following pages is shown by the example, 2(b)4. 2 stands for the main heading of the series; here it stands for the series dealing with "Experiments with Ferric Oxide and Ammonium Bromide." (b) serves to differentiate the experiments done under this heading. 4 stands for a slight variation of the experiment. Usually this entails changing a small amount of material or flow rate of gas. Upon seeing the third number, one should try to see a trend being formulated within the series. The series often involves a trial and error process in an attempt to find an optimun effect in accordance with the goal as stated in the purpose under the main heading. If no number is present after the letter the experiment was unique.

1. Experiments in a Helium Atmosphere

Purpose:

According to Kittaka and Kaneko in reference 6, iron whiskers were grown in great quantities by mixing $FeCl_2 \cdot 6\ H_2O$ or

$FeBr_2 \cdot 2\ H_2O$ with carbon black in ratios ranging from 1 to 100 weight per cent. However, the specific type of carbon black or charcoal used was not specified. Consequently the excellent results were not duplicated here, although the following types of charcoal were used: bone, NucHar C-190N, and Darco G-60. In the Japanese article the whiskers were grown in an atmosphere of air plus the gases given off by the starting materials.

The article concluded that the hydrogen reducing atmosphere was produced by reaction of carbon with water present in the charcoal followed by the growth reaction.

$$H_2O + C \longrightarrow H_2 + CO$$

$$\text{liq } FeX_2 + H_2 \rightarrow Fe + 2\ HX$$

The intention of the following series of experiments was to modify the reference experiment in order to explore the possiblity of using helium as a carrier gas for transportation of selected materials into the chamber in order to enhance whisker growth.

1(a). Experimental

3.0 g $FeCl_2 \cdot 4\ H_2O$ + 1.0 g NucHar C-190 brand charcoal were ground together with a mortar and pestle and placed in a quartz boat. The boat was placed within a 16mm diameter quartz tube approximately 10 cm long between two smaller iron boats filled with Darco G-60 brand charcoal. Helium flow was 0.15 CFH; time of reaction was ten minutes: temperature was 730°C.

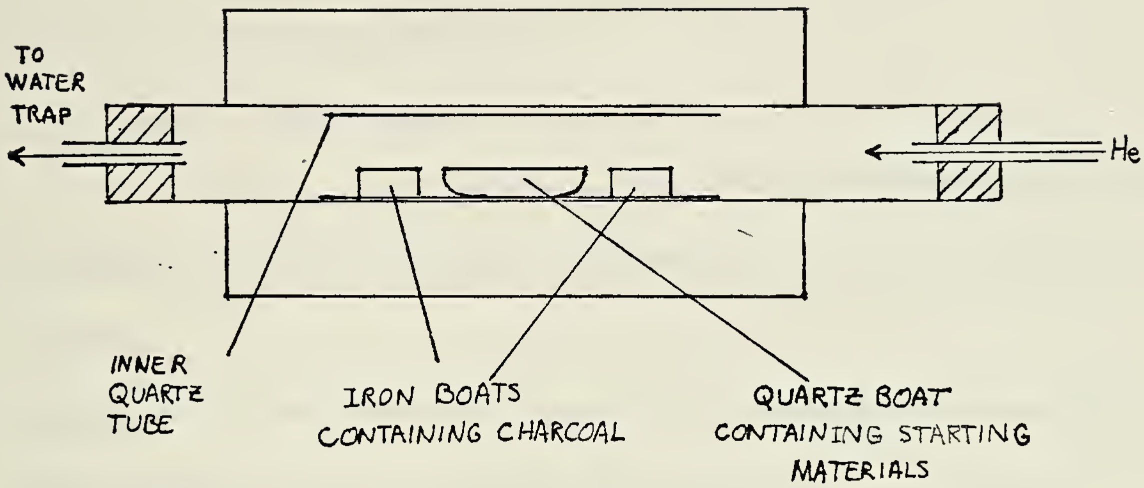



Fig. 3 Apparatus using carbon as a hydrogen source and heluim as a carrier gas.

Results: A fair number of short (1 - 2 mm) whiskers were grown, however, most of the metal was reduced as platelets. A white coating on many whiskers was also observed.

1(b). Experimental

The above experiment was modified by bubbling the He through two erlenmeyer flasks in order to moisten the atmosphere. Temperature = 730°C. Time = 10 minutes. He flow = 0. 2 CFH.

Results: The yield was very poor. No whiskers were formed; rather the metal was reduced as platelets approximately 0. 5 mm square.

It had been expected that the extra water in the atmosphere would increase the hydrogen concentration by:

$$C + H_2O \rightarrow CO + H_2$$

However, this was not effective.

1(c). Experimental

The above procedure was repeated with both charcoal boats upstream. He flow ≐ 0.15 CFH. Temperature = 730°C. Time = 30 minutes.

Results: A few whiskers were observed on the surface but none were found when the mass was probed. The appearance of the mass in the quartz boat ranged from powdery at the upstream end to granular at the downstream end. All whiskers grown appeared at the powdery upstream end. By placing both boats upstream of the starting material the hydrogen concentration was increased at that end as can be seen by the growth occuring at the upstream end. One may conclude the poor yield of experiment 1(b). was due to lack of hydrogen.

1(d). Experimental

3.0 g $FeCl_2 \cdot 4\ H_2O$ + 1.0 g NucHar C-190N charcoal was prepared as before and placed in a quartz boat. Directly upstream of the quartz boat was placed a small iron boat containing a ground charge of $FeCl_2 \cdot 4\ H_2O$. Furthest upstream was another but longer iron boat containing a charge of Darco. Helium flow rate = 0.2 CFH. Temperature = 800°C. Time = 11 minutes.

Results: No whiskers were in either boat. A few platelets were

formed in the quartz boat. Most of the $FeCl_2 \cdot 4\ H_2O$ charge had vaporized, however, a few flakes of reduced iron were present. The expected results had been that the extra source of $FeCl_2$ vapor would increase the growth, yet this was not the case.

Discussion:

Using helium as a carrier gas was not advantageous. The helium flow, as was observed in experiment 1(a)., did not drastically reduce the whisker growth as compared to growth in air. This was predictable since the reactions occurred in the charcoal mass at very short distances between hydrogen sources and growth sites such that the low velocity helium didn't displace the hydrogen before the growth reaction occurred.

There are two possible reasons for no enhancement of growth by introducting extra $FeCl_2$ vapor to the system as was done in experiment 1(d). First, the hydrogen source was so small as to create a very weakly reductive atmosphere. The other possibility was that the $FeCl_2$ must be in liquid from to react so as to form whiskers. Thus the $FeCl_2$ vapor did not react.

An overall factor that would influence the form of the iron produced would be the supersaturation of the halide vapor. It is generally believed (Ref. 3) that whiskers grow in vapors whose supersaturation ratios are not far in excess of 1.0. Introduction of foreign material such as water vapor could affect that ratio such that the iron is produced in a different form.

## 2. Experiments with Ferric Oxide and Ammonium Bromide Mixtures

Purpose:

It had been previously shown in this laboratory that a mixture of $Fe_2O_3$ and $NH_4Br$ could produce excellent yields of iron whiskers under a hydrogen atmosphere. The reaction was thought to be:

$$H_2 + 4NH_4Br + Fe_2O_3 \rightarrow 4NH_3 + 2\ FeBr_2 + 3\ H_2O$$

$$FeBr_2 + H_2 \rightarrow Fe + 2\ HBr$$

An undesirable characteristic of this particular mixture was that the whiskers were fastened securely to the substrate. Consequently the crystals were not easily removed. The following series of experiments was executed to find a method of growing iron whiskers which could be detached from the substrate and be relatively free from flaws. Two methods were used to accomplish this end. The first involved a series of experiments which examined the addition of a loose substrate to the starting material. Carbon which reacted in the environment was added, and then various inert materials were added to accomplish this goal.

The second method examined was the growth of whiskers on a surface not in contact with the starting materials. It was hoped that transporting the reactive vapors to sites not in contact with the original mass would lead to finding a site which would allow their removal.

2(a). Experimental:

To 11.0 g of ground $NH_4Br$, 7.0 g $Fe_2O_3$ was added, and the

mixture ground together in a mortar. (Henceforth this mixture will be called 7-11.) 3.0 g of this mixture was placed on an iron liner which was set into a quartz boat. The charge was reduced under a hydrogen atmosphere at a flow rate of 0.5 CFH at 730°C. for 13 minutes.

Results: A high yield of whiskers of varying sizes was obtained, the longest of which was over 1 cm. Growth often occurred in clumps along the sides of the liner. At the bottom of the liner the metal was reduced as a foil with some shorter whiskers growing out. Some of the whiskers were observed to have balls of material at their ends. This might have indicated a VLS mechanism. If this was the case then an impurity was present fulfilling the requirements of a nucleating site as stated in the previous discussion of VLS mechanism.

2(b)1. Experimental:

3.0 g of 7-11 was ground with 1.0 g of NucHar C-190N charcoal and the resultant mixture reduced with hydrogen. Temperature = 730°C. Hydrogen flow rate = 0.5 CFH. Time = 13 minutes.

Results: The mass was very powdery and the volume was greatly increased over that of the starting materials. A few whiskers were identifiable. When the mass was probed with a spatula, no whiskers were found below the surface.

2(b)2. Experimental:

The mass of charcoal was reduced to 0.25 g and the experiment rerun under the same conditions.

Results: The mass was very voluminous with the surface having

a metallic nature rather than charcoal as was seen in experiment 2(b)1. Some short whiskers were entwined in the mass at the surface. No whiskers were found below the surface.

2(b)3. Experimental:

3 g of 7-11 was ground with 0.1 g NucHar C-190N and reduced under the conditions of the previous experiment.

Results: The mass more closely resembled that of experiment 2(b)1. (where no charcoal was added) than that of experiment 2(b)2. where 0.25 g charcoal was present. However, the yield was not as great as in experiment 2(b)1. Most of the whiskers grew on the liner sides while the metal was reduced as a foil at the bottom. Several grew in clumps and were often bent or misshapen.

When these clumps were probed by a spatula carbon particles were found beneath the surface as well as a few whiskers. Beneath the foil at the bottom of the liner much carbon was found as well as a few metal particles.

2(b)4. Experimental:

Experiment 2(b)3. was performed using a charge of 3.0 g of 7-11 and 0.15 g of NucHar C-190N charcoal.

Results: Two types of whiskers were formed. On the sides long, thin whiskers were present attached to the melt. At the bottom of the liner a mixture of charcoal and metal was present with short whiskers disbersed throughout.

2(b)5. Experimental:

The experiment was repeated with 3.0 g of 7-11 and 0.12 g NucHar.

Results: The boat was tilted during the reduction, consequently, there was a hard melt on the lower side. On the upper side some very long thin whiskers grew from a powder mass. Charcoal was found beneath this mass.

2(c)1. Experimental:

A 3.0 g charge of 7-11 mixture was placed in the liner, and 0.12 g of NucHar was spread over the surface. Otherwise the conditions were the same.

Results: Three kinds of masses were present. The usual shiny metallic foil with carbon granules beneath had collected at the bottom. No whiskers were present here. Higher up the side of the liner a second type of mass was found having a gray powdery nature. This was a mixture of mostly carbon with metal. A few short whiskers were present. The third type of mass was situated above the second type on the side of the liner. A number of long whiskers were present and could be extracted relatively easily by using tweezers. A general observation was that the growth direction was perpendicular to the surface of the liner.

2(c)2. Experimental:

Experiment 2(c)1. was repeated. 3.0 g of 7-11 mixture was placed in the steel liner, and a large amoung of NucHar was sprinkled on the surface such as to give a thin coating over the entire surface.

Results: Overall, the entire mass was black with spots of metal coating on the surface. At the upstream end the mass was almost entirely carbon-like in appearance. As the mass went downstream it became more metallic in appearance. The yield of whiskers was not as great as that of experiment 2(c)1. with the number fewer, and the size shorter and wider. A few areas of powdery mass were present with some long whiskers growing out. When the entire mass was probed, much charcoal was found beneath along with some metal and no whiskers.

2(d). Experimental:

3.0 g of 7-11 mixture ground together with 0.25 g Darco G-60 brand charcoal. Temperature = 730°C. Hydrogen flow = 0.5 CFH. Time = 15 minutes. (Darco was a coarser more granular brand of charcoal. NucHar was a light, powder charcoal.)

Results: Most of the metal reduced was in the form of a foil in the bottom of the liner, while some clumps of metal were attached to the side. These small masses were hard and made up of carbon and metal granules. Many whiskers also grew from their surfaces, however, several whiskers were deformed.

2(e). Experimental:

3.0 g of 7-11 was ground together with 0.12 g NucHar. The hydrogen was bubbled through water before flowing into the chamber. Time = 10 minutes. Temperature = 730°C. Hydrogen flow = 0.5 CFH.

Results: At the upstream end there was a gray powdery mass as described in experiment 2(c)1. A few long whiskers as well as many short thick ones were present. At the downstream end was a metal foil where some long but deformed whiskers grew from carbon particles along the sides.

2(f)1. Experimental:

2.0 g of 7-11 mixture, 1.0 g $FeCl_2 \cdot 4\ H_2O$, and 0.12 g NucHar were ground together and reduced under hydrogen. Temperature = 730°C. Time = 12 minutes. Hydrogen flow rate = 0.5 CFH.

Results: The predominate mass was a shiny metal foil. Many long whiskers were growing from the sides where the substrate was more granular. Shorter whiskers were growing from the foil surface. Most of the carbon was found beneath the foil when the mass was probed. A few powdery, gray masses were present at the downstream end with whiskers growing from them.

2(f)2. Experimental:

Experiment 2(f)1. was repeated increasing the amount of NucHar to 0.2 g.

Results: The entire mass was a large powder "cloud" with a few short whiskers growing in the mass.

2(f)3. Experimental:

Experiment 2(f)2. was repeated several times varying the mass of NucHar only, with the following results:

Results: a. 0.15 g - A typical metal foil was formed.

b. 0.17 g - One powdery mass with a few short whiskers was observed.

c. 0.16 g - Here was a powdery surface containing a few long whiskers. The longer ones grew along the sides of the liner, and beneath the powdery surface was a metal foil with charcoal underneath. Some of the whiskers were very thin and only noticed when a ball was seen at their tip.

2(g). Experimental:

A series of experiments was performed with 1.5 g of 7-11, 1.5 g $FeCl_2 \cdot 4\, H_2O$, plus varying amounts of NucHar. Temperature = 730°C. Time = 13 minutes. Hydrogen flow = 0.5 CFH.

Results: 2(g)1. No charcoal added - a very large yield grew from the metal foil. In general the whiskers were very long and thick in diameter. The thickest growth (in number of whiskers per unit area) grew from the upper edge of the charge while the sparsest was along the bottom of the boat. Several clumps with whiskers growing out were on the liner sides. The whiskers were attached tightly to the substrate and not easily removed.

2(g)2. 0.2 g - a gray, powdery cloud with a few short whiskers was formed.

2(g)3. 0.12 g - a foil was along the bottom. Some long misshapen whiskers grew from fine granular masses on the sides. The masses were hard, and whiskers were not easily removed by tweezers.

2(g)4. 0.15 g - most of the metal produced was in the form

of a foil. The foil wasn't shiny; rather it was gray. Some very long whiskers grew from granular masses on the side of the liner, two of which were of such length that their growth was stopped when their tips touched the chamber wall.

2(g)5. 0.16 g - again most of the reduced metal was foil, however, present were a few fairly long whiskers which were easily removed from a gray mass situated along the upper edges of the boat.

2(g)6. 0.16 - the charcoal was first heated alone for 10 minutes under a hydrogen atmosphere at 730°C. Then the charcoal was mixed with the standard mixture of 7-11 and $FeCl_2 \cdot 4\ H_2O$. The resultant product contained three types of masses. At the upstream end the mass was light gray and powdery with no whiskers. The bottom was covered by a metal foil while a darker metallic region was present at the edge of the foil as well as in the downstream end. Whiskers grew in this region but were not easily removed.

2(h). Experimental:

A series of experiments was run using 1.5 g $FeCl_2 \cdot 4\ H_2O$ + 1.5 g of 7-11 ground together. The variable in the series was the amount of flake graphite added to the above mixture. Temperature = 730°C. Hydrogen flow = 0.5 CFH and time was 10 to 15 minutes. (Time was not an important parameter if all reductions were allowed at least 10 minutes to react.)

2(h)1. 0.21 g - a very large yield of long whisker was

obtained. However, it was not as large a yield as that observed when no graphite was present. Most were grown on the sides of the liner.

2(h)2. 0.42 g - most of the metal produced was in flakes, that is, the metal had formed a coating about the graphite flakes. Many short whiskers were along the upper edge of the liner as well as a few long ones. They were fairly easily removed as compared to the previous experiment.

2(h)3. 0.30 g - a larger number of whiskers were grown than in experiment 2(h)2. but less than 2(h)1. They were not as easily removed as in experiment 2(h)2.

2(i). Experimental:

A series of experiments was performed with the mixture of 1.5 g $FeCl_2 \cdot 4\ H_2O$ and 1.5 g of 7-11. This was mixed with several different inert materials in varying quantities in an attempt to find a substrate with which a good yield of whiskers could be obtained while allowing them to be easily removed. Temperature = 730°C. Hydrogen flow rate = 0.5 CFH. Time = 12 to 15 minutes.

Results: 2(i)1. 0.16 g NucHar + 0.30 g quartz powder - one large gray, powder cloud was obtained, with a few whiskers along the upper edges.

2(i)2. 0.10 g of NucHar + 0.30 g quartz powder - most of the metal was reduced as a foil, and some very long whiskers were growing in the direction of hydrogen flow.

2(i)3. 0.30 g quartz powder - the substrate was very

brittle and many whiskers were grown, however, these were securely fastened to the base.

2(i)4. 0.7 g iron filings - a good yield of long whiskers was present; the crystals were attached to a metal substrate and not easily removed. Many iron filings were found beneath the metal foil.

2(i)5. 0.7 g iron filings + 0.16 g NucHar charcoal - one large black cloud with a few short whiskers was obtained, and most of the metal was reduced to a gray foil over the charcoal. When this foil was probed two layers were found beneath. The upper layer was gray in color with metal grains reduced in the mass. The lower layer contained less metal and was darker in appearance. The iron filings were not found at the bottom of the liner as was the case in experiment 2(i)4. Also, compared with experiment 2(g)5, where no iron filings were used, the effect due to charcoal was enhanced. In that experiment the mass was largely a foil, while here it was less metallic.

2(i)6. 0.7 g iron filings + 0.10 g NucHar - most of the metal was in the form of a foil with a mixture of carbon and metal grains beneath the foil. One cannot distinguish by eyesight if these metal grains were formed by chemical reactions or were the iron filings in the starting materials. A powdery mass was at the upstream end with many whiskers growing there.

2(i)7. 1.0 g iron filings + 0.12 g NucHar - a metal foil was formed with a light, gray, powdery mass on its surface with some whiskers growing out. Many of these whiskers were easily removed with tweezers.

Discussion:

The previous sixteen procedures were performed with two purposes. First, it was to improve the yield of the 7-11. This was done by increasing the amount of reducible halide vapor with equal weights of $FeCl_2 \cdot 4\ H_2O$ and 7-11 mixture. The second purpose was to find a method of growing a good yield of whiskers on a substrate which would allow them to be easily removed.

This purpose was not accomplished by use of inert materials added to the mixture. It was found that the addition of any of the inert substances tested decreased the yield of the original mixture. In general it was observed that these inert substances were denser than the $FeCl_2$ melt. Consequently they sank to the bottom of the liner and were often found beneath a metal foil which had accumulated there.

Charcoal was an inert material as far as the growth reaction of iron whiskers was concerned. However, at 730°C it reacted by releasing water vapor. The amount of hydrogen produced by the reaction of carbon with water can be considered negligible compared with the hydrogen flow from outside the chamber. In general, there was a critical mass of charcoal that was added such that when less than this amount of carbon was added the result was a metal foil barren of easily removed whiskers. When an amount of charcoal in excess of the critical amount was added, the result was a voluminous mass with a few short whiskers. When an amount very near this critical value was

added as in experiment 2(g)5., the whiskers were relatively easy to remove. However, the yield was very low.

Taking an overall view of the entire series one can formulate several trends. The best whiskers grew on the liner sides. When the starting materials melted, growth sites were created as the edge of the melt retreated down the sides of the liner. The sites mentioned where whiskers were relatively easy to remove were due to carbon clinging to the sides and the growth occuring on their surfaces.

3. Growth of Iron Whiskers onto Various Surfaces.

Since there was very limited success in growing easily removable whiskers by mixing various materials within the starting materials, another approach was followed. Here an attempt was made to separate the growth sites from the starting materials by transplanting the vapor.

The first series of experiments dealt with the use of steel covers for the quartz boats. The reasoning here was that the vapor would reduce on the covers, and the whiskers possibly be removed from there. By experimentation it was hoped that a substrate could be applied to these surfaces and would accomplish this objective.

The second series of experiments dealt in growing whiskers on various sharp metal projections. Various procedures were were used here to find how whiskers grew from tacks and pins in different positions.

3(a)1. Experimental:

A charge of 7-11 mixture was placed in a steel liner which

was positioned in a quartz boat. The boat was covered with a flat steel plate with six, one-eighth inch holes drilled along the length of the plate. The cover was not air tight and would allow hydrogen to flow in under the edges of the plate as well as through the holes. Temperature = 750°C. Hydrogen flow = 0.5 CFH. Time = 30 minutes.

Results: Most of the metal was reduced in the form of a foil on the bottom of the steel liner. A fair yield of whiskers was obtained, however, it was inhibited as compared to a yield where the plate was not present. Many short whiskers were growing on the underside of the plate from very small sites which resembled crumpled bits of metal foil. High density of growth was found in and around the holes, while only one or two whiskers were found on the top surface around the holes. The whiskers attached to the plate were not easily removable with tweezers.

3(a)2. Experimental:

Experiment 3(a)1 was repeated under the same conditions with two, one-eighth inch holes drilled through the plate. However, the procedure was changed as follows: The chamber was purged with helium, and the boat placed in the hot part of the furnace for 15 minutes. Then the hydrogen was allowed to flow at 0.5 CFH. This was intended to have the starting materials melted and vapor starting to escape before the reducible atmosphere reached the boat. Then the vapor might be reduced while on the upper surface of the plate.

Results: Results weren't drastically changed from experiment 3(a)1.

Fewer whiskers grew on the underside of the plate with the highest density growth around the holes. Whiskers were present in the boat although the yield was less due to the $FeCl_2$ "boiling off" before the atmosphere became reductive. No whiskers grew on the upper surface of the plate.

3(b)1. Experimental:

2.0 g of 7-11 and 1.0 g $FeCl_2 \cdot 4\ H_2O$ were ground and placed in a metal liner. The metal liner was placed in a quartz tubing which was long enough to extend from the hot region of the furnace to the rubber stopper sealing the chamber off from the air as shown in the schematic.

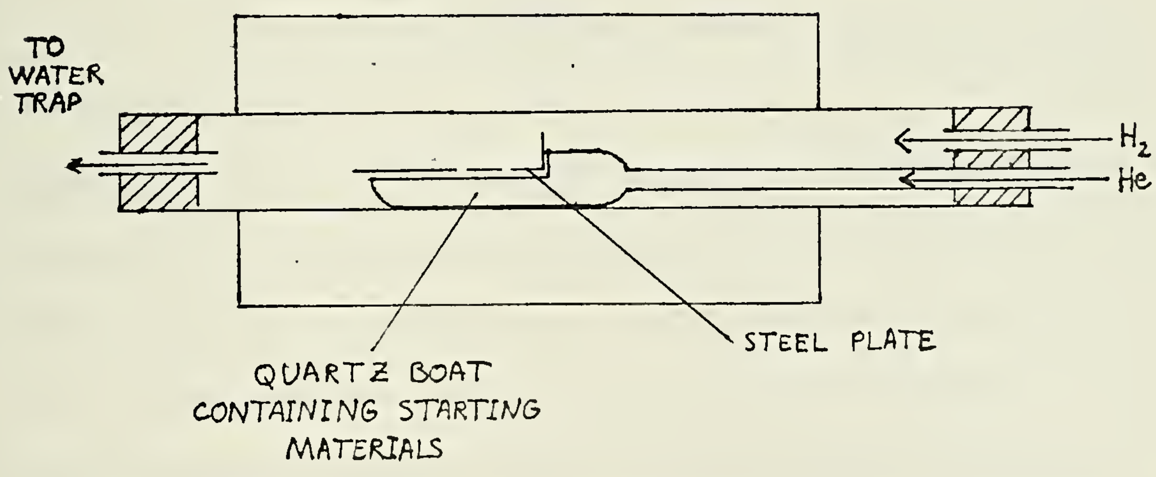



Fig. 4 Apparatus for experiments dealing in vapor transport.

Helium was passed into the quartz boat as shown while hydrogen flowed in the atmosphere of the chamber. The boat was covered by a steel plate as shown with two, one-eighth inch holes drilled through it. This

was done so that the vapor would flow through the holes onto the upper surface of the plate before coming in contact with the hydrogen. Temperature = 730°C. Time = 20 minutes. Hydrogen flow = 0.5 CFH. Helium flow = 0.2 CFH.

Results: Most of the iron was reduced in the boat with a yield which was very good despite the conditions. A few whiskers had grown on the bottom of the cover but were difficult to remove. In the holes there was a high density of short whiskers. No whiskers were on the upper surface of the plate. A light colored film was present on this surface and stayed in the same condition over a period of days. Over the same period of time, however, the bottom of the plate corroded.

3(b)2. Experimental:

The above experiment was repeated with helium flow increased to 0.3 CFH.

Results: The results were the same as those of experiment 3(b)1. except the yield was less while the whiskers were of the same character. After three days the extreme ends of the plate had a corrosion product on the upper surface as well as over the entire bottom surface. On the upper surface, the middle section of the plate between the holes and a short distance toward the ends on either side was clear of the corrosion. The film reported in experiment 3(b)1. was in this area.

3(b)3. Experimental:

The experiment was repeated with the following changes: The steel liner was shoved as far up the tubular part of the quartz

boat as possible instead of directly beneath the holes as before. This was to prevent the hydrogen from reacting with the vapor at the liner's surface so that it might excape to the upper surface of the plate. Helium flow = 0.5 CFH. Hydrogen flow = 0.4 CFH. Time = 30 minutes.

Results: No whiskers grew in the area covered by the tube, although a few did grow at the downstream end which was beneath the plate. Growth occurred on the upstream end of the bottom surface of the plate. Whiskers also grew in the upstream hole but not in the downstream one. A whitish film was present on the upper surface but no whiskers.

3(b)4. Experimental:

Experiment 3(b)3. was repeated with helium flow at 0.6 CFH and hydrogen flow of 0.2 CFH.

Results: No whiskers were in the steel liner under the tubular part. Very few were at the downstream end of the liner as well the underside of the plate. A few were in the upstream hole but none in the downstream hole.

3(b)5. Experimental:

Experiment 3(b)4 was repeated with the only change being a small amount of $Fe_2O_3$ was sprinkled on the upperside of the steel plate to provide possible whisker growth sites.

Results: Results were the same as those of the previous experiment with no whiskers grown on the top of the plate.

3(c). Experimental:

The conditions of experiment 3(b)5 didn't provide growth

sites on the upper surface for any possible escaping $FeCl_2$ vapor to react to form whiskers. Since growth sites occur on the bottom of the plate the following procedure was carried out: a liner containing just a charge of $FeCl_2 \cdot 4\ H_2O$ was set into the quartz boat. A steel plate was placed upside down over the liner as shown.

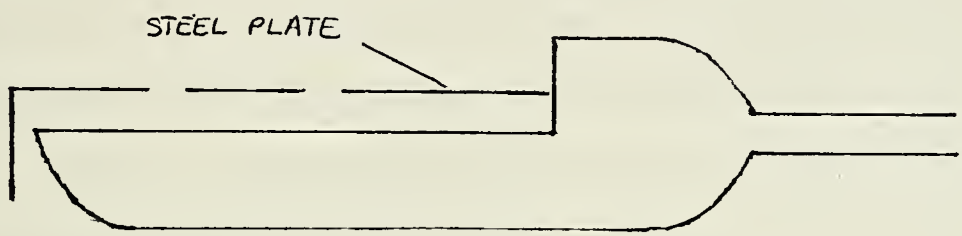



Fig. 5 Alteration of apparatus for experiment 3(c)

The quartz boat was placed in the hot part of the furnace for ten minutes under just a helium atmosphere. It was expected that the starting material would "boil" and possibly deposit some nucleating sites upon the plate.

Results: The expected small pieces of foil commonly seen on the underside of the plate in previous experiments were not present. Rather, the area was discolored possibly due to a film of material $FeCl_2$. One can say the small pieces of foil were deposited only when the materials were under a hydrogen atmosphere where the growth reaction was occurring.

3(d)1. Experimental:

Two tacks were positioned in a steel liner with their tips sticking up out of the charge of 3.0 g of $FeCl_2 \cdot 4\ H_2O$. The liner was placed in an open quartz boat and reacted under just a helium atmosphere flowing at 0.5 CFH. Time = 10 minutes.

Results: Many whiskers were grown on the liner walls along a line defined by the original limits of the charge's volume. A very dense growth was on the rodlike part of the tack. The whiskers grew in a radial direction like the spokes of a wheel growing from the hub. There was a sharp line of demarcation on the rod where whisker growth stopped, approximately where the surface of the original charge touched the vertical part of the tack.

3(e). Experimental:

A tack was placed in a charge of $FeCl_2 \cdot 4\ H_2O$ as before in experiment 3(d)2. The boat was placed in the hot part of the furnace ($730^{\circ}C$) under a helium atmosphere. Flow was 0.5 CFH. After 10 minutes the boat was withdrawn, and a film on the sides of the liner was observed as well as on the tack. Small crystals (not whiskers) were also on the body of the tack. A new tack was situated in the liner next to the other one. The boat was replaced in the furnace for 10 minutes with a hydrogen flow of 0.5 CFH.

Results: The whisker yield was poor but in the same areas as that of the previous experiment. Whiskers appeared on both tacks, but growth was more extensive, and the crystals longer on the tack that had been under both helium and hydrogen atmospheres.

Discussion:

Acceptable growth on the upper surface of the plate was not obtained. There were indications that $FeCl_2$ did, however, reach that surface and was reduced there. One may be able to conclude this from the noncorrosive film appearing near the holes. Iron whiskers in the boat and underside of the plate did not corrode with time. However, the steel liner and plate, which were not pure iron as were the whiskers, corroded. Thus, one may conclude the film on the upper surface was pure iron produced by reduction of $FeCl_2$. If this was true, then the situation was one where the reduction occurred in whisker form on one side of the plate and as a film on the other side.

Several reasons could be responsible for this phenomenon. The supersaturation ratio of $FeCl_2$ above the plate could be a value not conducive to whisker growth, or growth sites for whiskers may not be present on the upper surface. On the underside, whiskers grew from small pieces of material present due to the reaction of the starting materials.

This might be a future technique for studying nucleating sites. A series of experiments would have to be conducted such that starting materials would be subject to reductive conditions for a small interval, removed, observed, and replaced. A progression of nucleating site, whisker, and termination should be observed. This observation should be easier than trying to observe growth in the boat where sites are often covered by a film of metal.

The tack experiments seem to confirm that whisker sites tend to be above or follow the edge of the region bounded by the starting material. Whisker growth tended to be on the sides of the liner and on the upper part of the tack. This could show that a liquid film in the growth area cannot exceed a certain thickness, or it will poison the growth site.

Experiment 3(e) showed that the nucleating sites are not formed by just the initial heating of the starting materials, rather hydrogen may be necessary. Sites for growth could be found even after 10 minutes of heating $FeCl_2$ at 730°C under a helium atmosphere.

B. GROWTH OF COPPER WHISKERS

In reference 7 a method of growing large numbers of copper whiskers was discovered. The materials in the experiment were Cu0, CuCl, and graphite mixed in weight ratios of 100:10:5. Experiments were carried out in this article using a furnace similar to that used here to grow iron whiskers. The above starting materials were placed in a boat which was set inside a 16mm diameter quartz tube between two pieces of graphite. This tube was then fitted inside the larger diameter tube making up the furnace chamber. Both ends of the chamber were sealed by inserting solid rubber stoppers. Thus, the growth of whiskers occurred in an atmosphere of air and those gases accumulated from the reaction, CO and $CO_2$ in particular.

Pure copper in whisker form was thus produced by reduction of CuO.

$$2\,CuO + CO \rightarrow Cu_2O + CO_2$$
$$Cu_2O + CO \rightarrow 2Cu + CO_2$$

CuCl was also a source of copper metal reduced by hydrogen produced from water in the graphite.

$$H_2O + C \rightarrow CO + H_2$$

$$2\ CuCl + H_2 \rightarrow 2\ Cu + 2\ HCl$$

$$2\ HCl + Cu_2O \rightarrow 2\ CuCl + H_2O$$

This method of whisker growth was of special importance due to the reported very high yields. Copper was said to have been produced in whisker form at nearly 100 percent of the theoretical yield.

1(a). Experimental:

3.0 g CuO (powder), 0.3 g flake graphite, and 0.15 g CuCl were ground together and reduced as described above. These amounts were the weight ratios of 100:10:5 as prescribed by the reference article. The apparatus was modified as follows: (1) Instead of graphite, iron boats were filled with Darco brand charcoal and used to supply the reductive atmosphere. (2) The gas was allowed to escape into a water trap upon expanison. Time = 20 minutes.

Results: No whiskers were detected. The surface of the mass was black and the interior contained red particles which were probably unreduced $Cu_2O$. On the metal liner was a copper colored film covering almost the entire surface.

1(b). Experimental:

6.0 g CuO (wire form), 0.6 g flake graphite and 0.3 g CuCl were ground together and used as starting materials. Temperature = 730°C. Time = 20 minutes.

Results: The results were the same as those of experiment 1(a). Much of the CuO hadn't been reduced to $Cu_2O$ which was present as red grains. One could determine this because CuO was still in the distinguishable pellet form in which it had been before heating.

1(c). Experimental:

3.0 g CuO (powder), 0.3 g NucHar C-190 brand charcoal, and 0.15 g CuCl were the starting materials. Temperature = 730°C. Time = 20 minutes.

Results: The mass resembled one homogeneous, voluminous "cloud" throughout. Looking with the naked eye the appearance was one of copper powder. When seen under the stereomicroscope at 30 power one was able to see a network of very small whiskers entwined throughout the mass. The mass was held together such that when probed with a spatula, the entire "cloud" would move.

1(d). Experimental:

3.0 g CuO (powder), 0.3 g Darco, and 0.15 g CuCl were the starting materials. Darco was a coarser, more granular charcoal as opposed to the powdery NucHar used in 1(c).

Results: The mass closely resembled that of experiment 1(c). and that reported in the literature (Ref. 7). Some "balls" containing many whiskers were observed. When penetrated, the mass was seen to assume more of a charcoal nature with depth.

1(d)2. Experimental:

3.0 g CuO (wire), 0.3 g Darco, and 0.15 g CuCl were reduced under the previous conditions.

Results: The cloud was more voluminous and of a more copper color. No charcoal was on the surface as was observed previously. Whiskers were below the surface, however, as the mass was probed deeper the yield of whiskers decreased and the mass assumed more of a charcoal character.

1(d)3. Experimental:

3.0 g CuO (powder), 0.48 g NucHar, and 0.15 g CuCl were reduced for 20 minutes at 730°C.

Results: A yield no higher than that of 1(d)2. was obtained. The mass was of a harder, cakey nature than before.

1(e)1. Experimental:

3.0 g CuO (powder), 0.3 g Darco, and 0.15 g CuCl were reduced at 700°C for 41 hours.

Results: There was high whisker yield, but the mass was essentually of the same voluminous nature.

1(e)2. Experimental:

Experiment 1(d)4 was repeated at 600°C.

Results: The yield was the best obtained thus far, and it was easier to detect the strands of whiskers by the naked eye. The whiskers had a shinier copper color compared to those grown at temperatures in excess of 700°C. Still, the whiskers are entwined and difficult to separate.

1(e)3. Experimental:

Experiment 1(e)1 was repeated at 500°C for 22.5 hours.

Results: No perceptible improvement or decrease in yield was obtained.

1(e)4. Experimental:

Experiment 1(e)1 was repeated at 400°C for 12 hours.

Results: Very poor whisker growth was observed, but, some very small diameter whiskers were observed such that they were only noticed when light refelected from them. Only a small percentage of starting material reacted. When the surface was disturbed by probing more whiskers could be detected by the reflection of light.

1(e)5. Experimental:

The experiment was repeated at 336°C for 48 hours.

Results: A low yield was obtained, however, some very small diameter whiskers which were easily removed were observed. These were longer than those obtained at higher temperatures.

1(e)6. Experimental:

The temperature was raised to 430°C and the same mixture of new material was reduced for 18 hours.

Results: A typical entwined, high yield was obtained. Many "balls" of tangled whiskers were observed. A few whiskers were long, straight and untangled such that they could be removed by the use of tweezers.

1(f)1. Experimental:

3.0 g CuO, 0.6 g Darco, and 0.15 g CuCl were placed in a furnace at 750°C under standard procedures for one hour. However, the usual two accompanying boats of Darco were not used to produce the reductive atmosphere.

Results: Many isolated areas of tangled whisker growth were present on a surface predominately charcoal in nature. A few longer, straight whiskers were present. When the surface was disturbed more whiskers were observed when their movement reflected light. The growth below the mass was of the same nature.

1(h). Experimental:

A charge of 3.0 g CuO, 0.3 g Darco, and 0.15 g CuCl was prepared and reduced under the following schedule:

1(h)1. 15 hours at 330°C.

1(h)2. 11 hours at 370°C.

1(h)3. 14 hours at 540°C.

After each period of reduction, the inner quartz tube containing the quartz boat and two iron boats was removed, and the growth observed. New Darco was placed in the iron boats between each period, but the same charge of starting materials was used throughout. This was done to find how the growth progressed as the mixture was heated.

Results: 1(h)1. A low yield of tangled whiskers was observed at each end of the boat. A few short, straight whiskers were in the middle section of the mass. Possibly the tangled growth could have been due to the proximity of the charcoal boat to these areas.

1(h)2. The yield became greater. When a draft of air was directed at the surface, one could see small diameter whiskers by light reflection. Otherwise, they were difficult to see. These whiskers were seen in the middle section which was beginning to acquire areas of

tangled growth. Both ends of the mass were covered by whiskers entwined in clumps. The small diameter, straight whiskers could have been present but obscured by the other type of growth.

1(h)3. The mass was of the typical high yield appearance expected at this temperature. Clumps of tangled whiskers were observed over the entire surface, while the small, straight whiskers could not be observed.

1(i). Experimental:

1(i)1. 3.0 g CuO, 0.3 g Darco, and 0.15 g CuCl were reduced for 10 hours with no end boats containing charcoal. The temperature was the lowest used in the growth of copper whisker at 316°C.

1(i)2. The very same mixture was heated at 380°C for 21 hours after its appearance had been noted.

1(i)3. The appearance was noted, boat placed in the furnace again, and reduced at 730°C for 2.5 hours. No end boats were used for extra charcoal.

Results: 1(i)1. A few short but straight whiskers were grown. Two relatively long ones were present on the sides of the liner. Whiskers growing on the surface were easily removed by tweezers.

1(i)2. There was little more whisker growth. Some tangled clumps appeared in the middle section.

1(i)3. The tangled growth increased, but the yield was still low. Some red crystals were present indicating $Cu_2O$ that had yet to be reduced to Cu. No increase in short, straight whiskers was observed.

1(j). Experimental:

A fresh mixture of the materials used in experiment 1(i) was reduced without end boats at 730°C for one hour.

Results: The typical high yield of entwined copper whiskers was obtained.

Discussion:

The reaction did not occur using graphite as reported in the literature, however, both types of charcoal used were successful. Perhaps the Japanese authors made a mistake in translation. Best results were obtained at a temperature of 600°C.

The high yields reported in the literature were duplicated. However, these yields were of a tangled nature, not easily separated, or of the desired straight and thin appearance. it was possible to obtain this growth at lower temperatures, but at the same time, yield was drastically reduced and time of reaction increased.

The concentration of the reductive gases, $H_2$ and CO, was of importance. At lower temperatures the production of these gases would decrease while at the same time the straight thin whiskers appeared. Also, at lower temperatures tangled growth appeared at the ends of the mass which would be in closer proximity than the center where the desirable forms appear. This could allow one to predict that in a highly reductive atmosphere tangled, unrestrained growth occurs, while the more perfect whiskers appeared in less reductive atmospheres. This is a common generality of crystallization where the most perfect

crystals grow at slower rates. As added evidence for this idea, the electron scanning miscroscope showed very few of the perfect whiskers in mixtures grown with iron boats containing extra charcoal. If a mixture of tangled growth and perfect whiskers was present and undetected under the visual microscope, the high magnification of the instrument should have detected many of these perfect whiskers.

A suggested series of experiments to detect the role of CuCl in the mechanism will now be proposed. The effect of the amount of CuCl added should first be determined by varying the amount present. Since the reduction of CuCl depends upon the production of hydrogen obtained from the reaction of water and carbon, one would suspect that the small amount of water present would quickly react or evaporate away at 800°C. Thus the hydrogen supply is limited and appears only in the initial stages of the experiment. Therefore, could this mean that the reduction of CuCl is the initiating reaction producing the growth sites? To prove this, it might be productive to react the starting materials under a hydrogen atmosphere with carbon that had been heated previously under helium to remove water. The only reaction occurring should by the production of Cu by reducing CuCl. The mass should be examined carefully to see if this is so. Then reduce this same mass under an atmosphere of air and try to detect if growth was initiated from the sites produced by CuCl reduction.

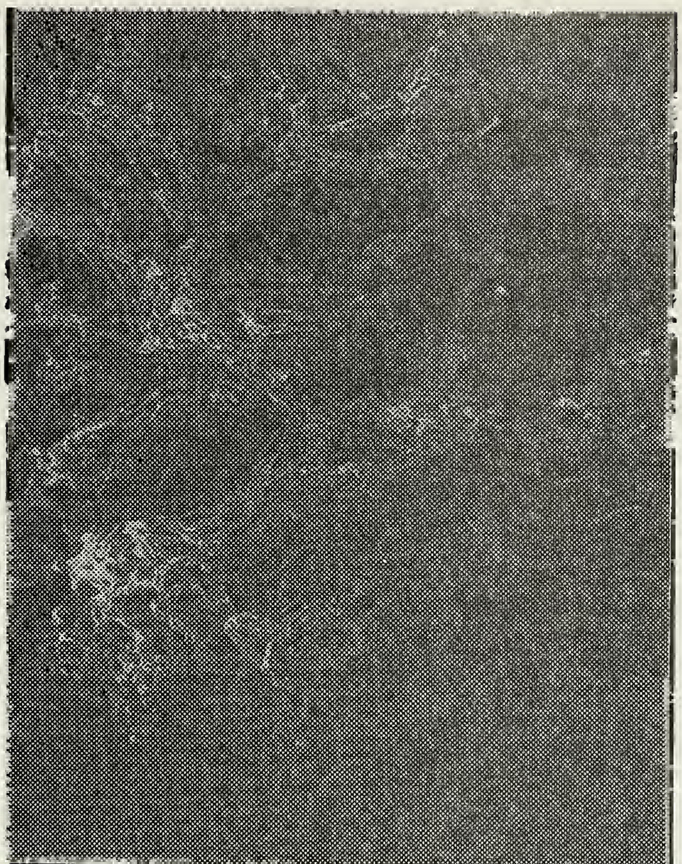


Fig. 6

Typical copper whisker growth (200x)

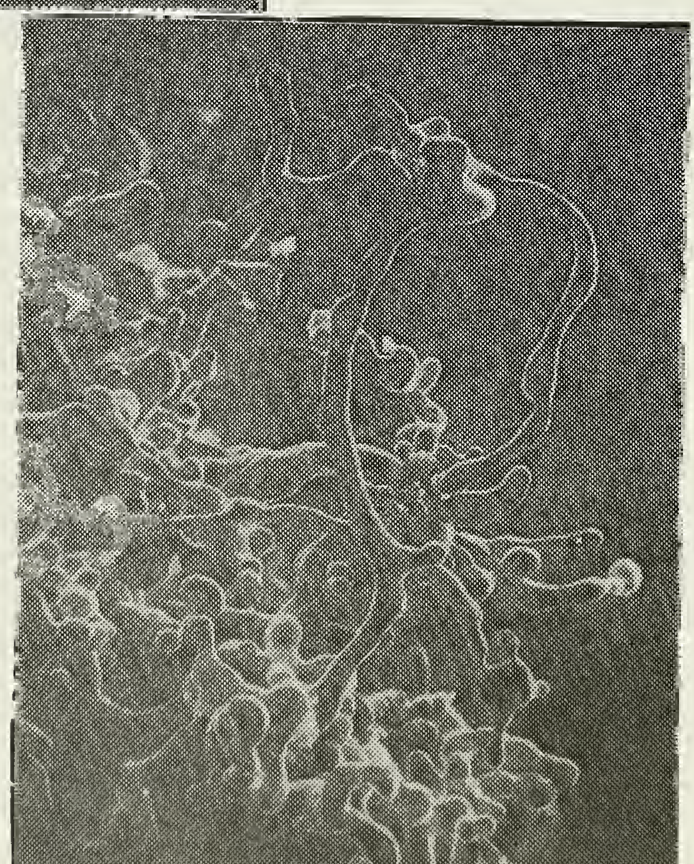


Fig. 7

Copper whiskers grown at 700°C. (500x)

## IV. COLD TIP THEORY

### A. POSTULATED MECHANISM

The VLS mechanism has had sound experimental evidence to prove its validity. However, this mechanism was applied only to nonmetals due to the lack of a suitable low melting alloy to serve as the condensing site for the iron whiskers.

The screw dislocation theory has never been conclusively proven to be the mechanism for growing pure metallic whiskers. Much controversy has surrounded the second mechanism. A screw dislocation would be very difficult to detect due to its very size, also, this dislocation would be very difficult to detect under the theory that growth stops when the dislocation disappears. Field emmission microscopy (Ref. 8) and electron scanning microscopes have to date failed to show conclusive evidence of screw dislocations.

The screw dislocation mechanism for metallic whiskers has had extensive mathematical treatment by Burton, Cabrera, and Frank in Ref. 4. Mathematics of diffusion controlled whisker grown from the vapor also has been given considerable attention (Ref. 9, 10), while heat flow in whiskers has been relatively ignored. The cold tip mechanism, as postulated in this paper, is valid only for endothermic reactions occurring on the whisker surface. As the reaction proceeds, heat is drawn from the material. The point of highest curavature, which is at the tip, will have the most heat withdrawn per unit volume.

Consequently, the temperature of the tip will be the coolest part of the whisker.

The reaction material is adsorbed on the surface of the whisker or a liquid film creeps up from the base and diffuses to the region of lowest energy on the whisker. In the screw dislocation mechanism, this region of lowest energy is the dislocation. However, a cold tip would serve the same purpose by removing energy from the diffusing material and thus decreasing its ability to translate to a different part of the whisker or evaporate to the atmosphere. There is a higher probability of finding reaction material at the tip, thus the reaction is more likely to occur in that region. Since the reaction is endothermic, more heat will be withdrawn from the tip and the tip will be cooled to an even greater extent. This phenomenon of a colder and colder tip is referred to as thermal runaway.

A mechanism where the heat flow is the important consideration has been proposed previously to explain dendritic growth from solutions (Ref. 15). Due to the heat of crystallization, there is a heat flux into a cubic crystal. The corners and to a lesser extent the edges are able to dissipate the heat more easily than the flat surfaces. Consequently the sides of the cube will accumulate heat faster than the edges and corners. This will be an important factor if the material has a low thermal conductivity. Otherwise this phenomenon of geometry will be offset by the heat being rapidly distributed throughout by conduction. For the case of low conductivity, growth will be stimulated at the

corners and to a lesser extent the edges. Thus, growth will be rapid at the eight corners and approach zero at the faces of the crystal. This complements the cold tip mechanism very well where the growth is even more directionalized due to the growth reaction being endothermic rather than exothermic as in the dendritic growth.

Since the reaction must be endothermic, one is able to analyze the nature of the reacting materials at the growth site. For iron whiskers growing at a typical growth temperature of 1000°K the reaction is:

$$FeCl_2 + H_2(g) \rightarrow Fe(s) + 2\ HCl(g)$$

Where the phase of $FeCl_2$ is unspecified to make the following points: (Ref. 16)

(1) If $FeCl_2$ is in the gaseous phase, the reaction is exothermic by approximately 6,000 calories per mole.

(2) If $FeCl_2$ is liquid, the reaction is endothermic by approximately 24,000 calories per mole.

(3) If the above reaction were to occur on another area of the whisker, and an iron atom formed in the liquid phase, it may then migrate to the tip. The reaction at the growth site would then be exothermic due to the heat of crystallization of Fe.

All three of the above cases could occur within the framework of screw dislocation theory, but case two is the only one which would lead to a cold tip. In addition, the first case where the $FeCl_2$ vapor reacts directly at the tip is rendered less likely by the equilibrium constant; at 1000°K the reaction is to the left. A similar reaction occurs

for copper whiskers and the three cases correspond to those shown above.

With $FeCl_2$ in the liquid phase, other effects of the cold tip can be noted. If the $FeCl_2$ tends to condense on the vertical part of the whisker before diffusing to the tip this region is heated by the heat of vaporization along the sides thus decreasing the chance or reaction in this area. The tip is thus colder relative to the sides. A colder tip will cool the atmosphere around it condensing $FeCl_2$ which releases the heat of vaporization destroying or at least decreasing the temperature of the tip. The tip would become less attractive as a reaction site compared to the sides. Consequently the whiskers would react uniformly over the surface until the cold tip was restarted by the endothermic reaction and the heat flow due to the high curvature at the tip.

A more probable prediction based on the $FeCl_2$ condensation would be that an equilibruim state would be reached such that the heat flux into the tip by condensation and convection equal heat removed by chemical reaction. The temperature at thermal equilibruim would still be substantially less at the tip compared to the sides of the whisker to insure preferential growth at the tip.

A different scheme of transport of liquid $FeCl_2$ postulates that the material diffuses from the base where it is present as a melt. The liquid is "hot" relative to the metal in that it is nearly the temperature of the substrate. As it advances, the sides of the whisker are heated, and the tip becomes cooler relative to the sides. This would tend to be

dominating effect when the whisker is short. As the whisker becomes longer the liquid from the base has further to travel. The whisker near the substrate would approach the temperature of the base due to its distance from the cold tip and proximity to the base. Consequently the liquid film would tend to evaporate from the sides once the tip has grown a certain distance from the base unless the atmosphere was supersaturated. This would be one explanation of why the atmosphere must be at least slightly supersaturated for whisker growth.

Summarizing, the effects of transport of liquid gives the following insight into whisker growth by the hypothesized cold tip mechanism. Growth is initiated by a nucleating site on the substrate. This site does not necessarily have to be a cool area but must be an area conducive to crystallization. Initial growth is due to liquid from the melt diffusing up the whisker sides. An intermediate period of growth occurs with a cool tip at a thermal equilibrium between the endothermic reaction and exothermic condensation. Finally, growth is terminated when the atmosphere is less than saturated and vaporization of the liquid occurs faster than it is supplied. This terminating situation would occur when the whisker has grown above the halide vapor or when that vapor has simply been depleted from the starting materials.

A very rough mathematical approximation for the temperature gradient can add a degree of rigor to the qualitative predictions. Suppose iron was formed by the liquid $FeCl_2$ reacting with hydrogen over an area of one square centimeter and grew a crystal from that surface at

$100\,\mu$/sec. In 100 seconds, 1 cubic cm would have been deposited at a heat of reaction of approximately -3500 calories. If this heat was supplied through just the tip by conduction from the metal one could predict:

$$q = -k\,A\,\frac{\partial T}{\partial x}$$

$q$ = rate of heat transfer. $\left(-3500\,\frac{\text{cal}}{100\ \text{sec}}\right)$

$k$ = thermal conductivity. $\left(0.16\,\frac{\text{cal}}{\text{sec}\ {}^{\circ}\text{C cm}}\right)$

$\frac{\partial T}{\partial x}$ = temperature gradient. $\left(\frac{{}^{\circ}\text{C}}{\text{cm}}\right)$

$A$ = area ($1\ \text{cm}^2$)

Solving for $\frac{\partial T}{\partial x}$:

$$\frac{\partial T}{\partial x} = 219\ \frac{{}^{\circ}\text{C}}{\text{cm}}$$

Or, over $100\,\mu$ the temperature difference between base and tip is 2.2 °C. This figure is very approximate and represents the greatest temperature gradient possible taking into account just heat transfer entirely through the tip. However, this calculation shows the tip could be significantly cooler than the rest of the whisker.

## B. THE MATHEMATICS OF HEAT FLOW

### 1. Differential Equations to be Considered

Before the whisker can be modelled, it is necessary to examine the differential equations describing heat flow. A very clear explanation of basic heat flow equations is given in reference 11.

For pure conduction in any material, the heat flows with the temperature gradient $\frac{\partial T}{\partial x}$ from an area of higher temperature to a lower

temperature region This is expressed by Fourier's law:

$$q = -kA \frac{\partial T}{\partial x}$$

Where: $q$ = Heat transfer rate.

$k$ = Thermal conductivity.

$A$ = Area.

$T$ = Temperature.

$x$ = Distance coordinate.

In three dimensions the equation for the unsteady state condition, that is the change of temperature with time is:

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}}{k} = \frac{\rho c}{k} \frac{\partial T}{\partial t}$$

Where: $q$ = Energy generated per unit volume.

$\rho$ = Density of the material.

$c$ = Heat capacity of the material.

Since the problem under consideration does not have a heat generating factor the equation becomes:

$$\nabla^2 T = \frac{1}{\alpha} \frac{\partial T}{\partial t}$$

Where: $\alpha = \frac{k}{\rho c}$ and is called the thermal diffusivity for a specific material.

Another important relationship used in heat transfer is Newton's law of cooling due to convection:

$$q = hA(T_W - T_\infty)$$

Where: $h$ = Film conductance whose units are heat per unit time, area, and degree of temperature.

$T_W$ = The temperature of the material at the boundary.

$T_\infty$ = The temperature of the fluid flowing by the solid boundary at a distance such that its temperature is unaffected by the solid's temperature.

h is not a constant for any material. It depends on geometry, velocity, and other variables and must be determined experimentally for each circumstance.

Another type of heat transfer needed to be examined for the problem under consideration is radiation. The net transfer of energy between two black bodies at temperatures $T_1$ and $T_2$ is described by the Stefan - Boltzmann law:

$$q = \sigma A (T_1^4 - T_2^4)$$

Where : $\sigma$ = The Stefan - Boltzmann constant.

This law is only valid for perfect emitters, therefore, to describe "gray" bodies compensating proportionality constants are used.

2. Finite Difference Techniques

In the analysis of heat flow, the temperature of a point depends upon all the points in its universe. Several complicating factors are found in the growth of whiskers in relation to the heat flow. The geometry of the boundary, as well as the boundary conditions, and the movement of the boundary due to deposition of material make the solution very difficult by analytical techniques. Consequently, the problem

is more conveniently solved using finite difference techniques (Ref. 12). This method substitutes discrete values to represent the continuous variable in its assigned region. In the problem under consideration, it is desired to relate a temperature with its position on the whisker. To do this a grid was superimposed over the shape and temperatures assigned to the grid points. The convention for the grid on the whisker was as follows: the central axis of the rod was called the y axis. The whisker was assumed to have cylindrical symmetry with the x axis representing the radial distance from the center. Thus the plane examined in this paper was that defined by the central axis and a line perpendicular to that axis extending to the surface of the whisker (Fig. 6). With a grid now superimposed, one may derive suitable relationships called difference equations for the mathematical analysis.

Calculations involving finite differences depend on replacing the differential equation with a difference equation. A difference equation approximates the differential equation by relating a set of points on the grid in a manner specified by the differential equation. This set of points is called a molecule and the differential equation to be solved in this paper is Fourier's law of heat conduction.

Some basic finite difference equations which are relative to the differential equation can be seen from Figure 7 where $\Delta$ is the unit grid size.

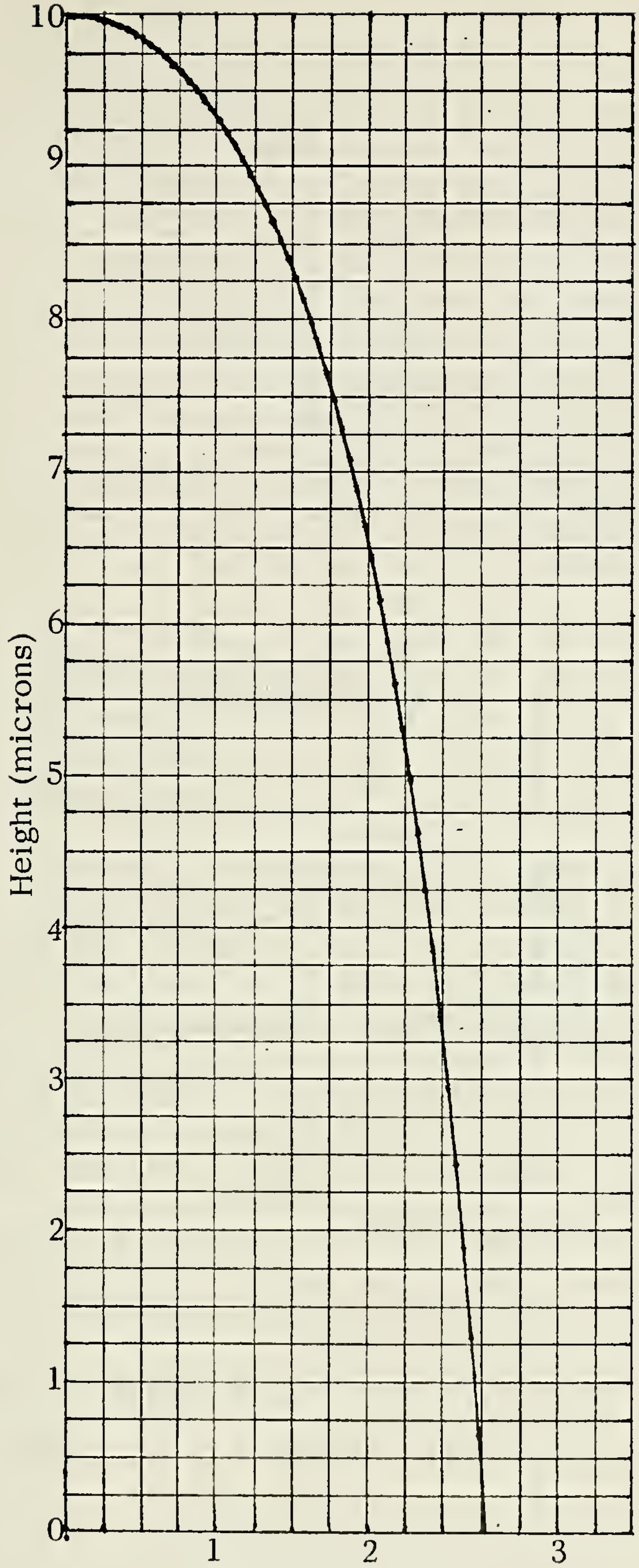



Fig. 8

Whisker and its grid overlay

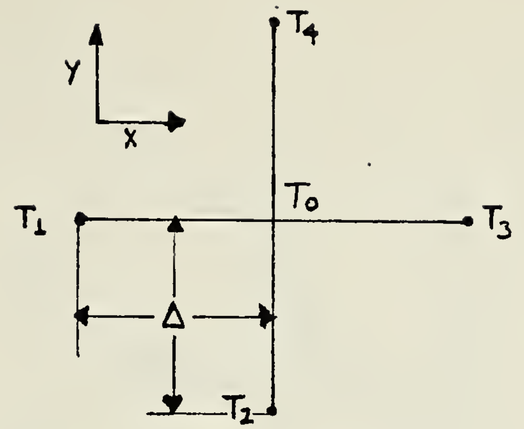



Fig. 9 Finite difference relationships

These equations evaluated at $T_0$ are:

$$\frac{\partial T}{\partial x} = \frac{T_3 - T_1}{2\Delta} \qquad \frac{\partial T}{\partial y} = \frac{T_4 - T_2}{2\Delta}$$

$$\frac{\partial^2 T}{\partial x^2} = \frac{T_3 - 2T_0 + T_1}{\Delta^2} \qquad \frac{\partial^2 T}{\partial y^2} = \frac{T_4 - 2T_0 + T_2}{\Delta^2}$$

However, these relationships only hold for grids of constant $\Delta$. In the shape under study, a complicating factor arises when the irregular boundary intersects the lines of the grid between points. A difference expression for the first and second partials of temperature with respect to nonuniform distances can be derived as follows:

Consider the grid with the boundary as shown.

Where: $\Delta$ = the size of the unit grid.

$P_j\Delta$ = the distance from point 0 to point j. In the above case it can be seen $P_1$ and $P_2$ are 1.0 $P_3$ and $P_4$ are fractions.

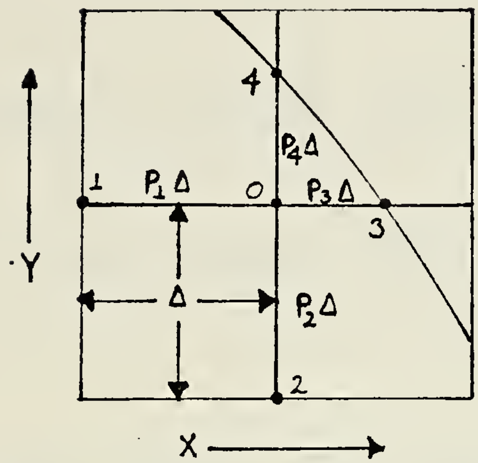



Fig. 10 An irregular boundary and grid.

The differential equation contains the expressions $\frac{\partial^2 T}{\partial x^2}$, $\frac{\partial^2 T}{\partial y^2}$, and $\frac{\partial^2 T}{\partial z^2}$ for which substituting expressions are derived as follows:

First expand $T(x_o + A,\ y_o)$ and $T(x_o,\ y_o + B)$, about $(x_o,\ y_o)$ which are the coordinates of point 0, by use of a Taylor series.

$$T(x_o + A,\ y_o) = T(x_o,\ y_o) + A\frac{\partial}{\partial x}\ T(x_o,\ y_o) + \frac{A^2}{2}\ \frac{\partial^2}{\partial x^2}\ T(x_o,\ y_o) + \ldots$$

$$T(x_o,\ y_o + B) = T(x_o,\ y_o) + B\frac{\partial}{\partial y}\ T(x_o,\ y_o) + \frac{B^2}{2}\ \frac{\partial^2}{\partial y^2}\ T(x_o,\ y_o) + \ldots$$

Substituting $A = P_3\Delta$ and then $A = -P_1\Delta$ into equation one as well as $B = P_4\Delta$ and then $B = -P_2\Delta$ into equation two, the following equations are obtained after truncating the rest of the terms in the series.

$$T(x_o + P_3\Delta\,,\ y_o) = T(x_o, y_o) + P_3\Delta \frac{\partial}{\partial x} T(x_o, y_o) + \frac{(P_3\Delta)^2}{2} \frac{\partial}{\partial x^2} T(x_o, y_o)$$

$$T(x_o - P_1\Delta\,,\ y_o) = T(x_o, y_o) - P_1\Delta \frac{\partial}{\partial x} T(x_o, y_o) + \frac{(P_4\Delta)^2}{2} \frac{\partial}{\partial x^2} T(x_o, y_o)$$

$$T(x_o, y_o + P_4\Delta) = T(x_o, y_o) + P_4\Delta \frac{\partial}{\partial y} T(x_o, y_o) + \frac{(P_4\Delta)^2}{2} \frac{\partial}{\partial y^2} T(x_o, y_o)$$

$$T(x_o, y_o - P_2\Delta) = T(x_o, y_o) - P_2\Delta \frac{\partial}{\partial y} T(x_o, y_o) + \frac{(P_4\Delta)^2}{2} \frac{\partial}{\partial y^2} T(x_o, y_o)$$

Solving the first two equations simultaneously and setting $T_j = T(x_j, y_j)$ the expression for the second partial of temperature in the x direction at point 0 is derived.

$$\frac{\partial^2 T_o}{\partial x^2} = \frac{2}{\Delta^2} \frac{1}{P_3^2 + P_1 P_3} \left[ T_3 - T_0 \left(1 + \frac{P_3}{P_1}\right) + \frac{P_3}{P_1} T_1 \right] \qquad (1)$$

$$\frac{\partial^2 T_o}{\partial y^2} = \frac{2}{\Delta^2} \frac{1}{P_3^2 + P_2 P_4} \left[ T_4 - T_0 \left(1 + \frac{P_4}{P_2}\right) + \frac{P_4}{P_2} T_2 \right] \qquad (2)$$

An expression for $\frac{\partial^2 T}{\partial z^2}$ can be found by examining Laplace's equation in terms of r, $\theta$, y where : (Ref. 13)

$$x = r\cos\theta$$

$$z = r\sin\theta$$

$$y = y$$

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} + \frac{\partial T}{\partial r} + \frac{1}{r^2} \quad \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial y^2}$$

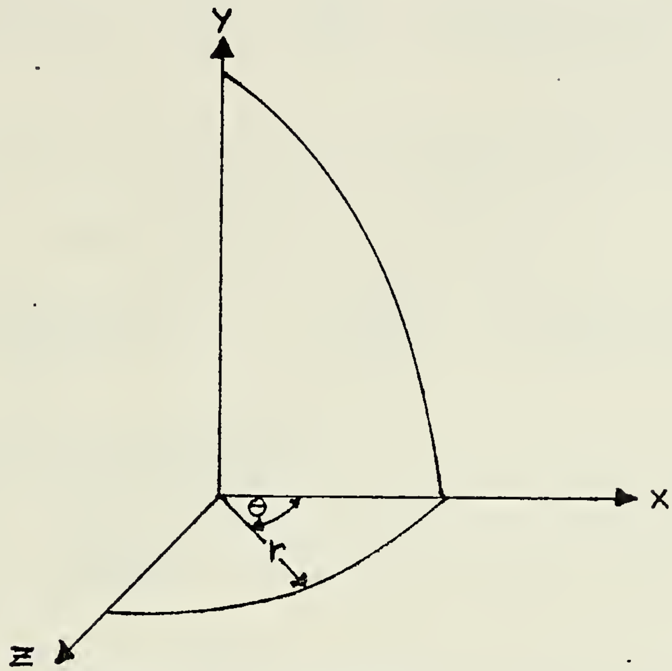



Fig. 11 Whisker in cylindrical coordinates.

Due to the cylindrical symmetry of the whisker $r = x = z$, and the problem can be analyzed in just the $x - y$ plane where $\theta = 0$. Laplace's equation thus reduces to :

$$\frac{\partial^2 T}{\partial z^2} \quad \frac{1}{x} \quad \frac{\partial T}{\partial x}$$

Substituting this relationship into Fourier's law, the conduction equation becomes:

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{1}{x}\frac{\partial T}{\partial x} = \frac{1}{\alpha}\frac{\partial T}{\partial t} \tag{3}$$

Difference equations for the first partial of temperature with respect to x can be derived by simulanteously solving the same Taylor series expansions used to derive equations (1) and (2). This results in:

$$\frac{1}{x}\frac{\partial T}{\partial x} = \frac{P_1 \; P_3}{x\,\Delta\,(P_1 + P_3)}\left[\frac{T_3}{P_3^2} - \frac{T_1}{P_1^2} - T_o\left(\frac{1}{P_3^2} - \frac{1}{P_1^2}\right)\right] \tag{4}$$

Notice that for points not adjacent to the boundary the fractions $P_1$, $P_2$, $P_3$ and $P_4$ are 1.0. Equations (1) and (2) reduce to:

$$\frac{\partial^2 T}{\partial x^2} = \frac{T_1 - 2T_o + T_3}{\Delta^2} \qquad \frac{\partial^2 T}{\partial y^2} = \frac{T_2 - 2T_o + T_4}{\Delta^2}$$

and equation (4) reduces to:

$$\frac{\partial T}{\partial x} = \frac{T_3 - T_1}{2\,\Delta}$$

For the study of unsteady state heat the following convention in nomenclature is followed:

$T_j$ = Temperature at point j.

$T_{j,+1}$ = Temperature at point j at one time interval later.

Using Fourier's law of conduction assuming no heat source within the element:

$$\nabla^2 T = \frac{1}{\alpha}\frac{\partial T}{\partial t}$$

the temperature one interval can be calculated.

$$\frac{\Delta T}{\Delta t} = \alpha \nabla^2 T$$

$$\Delta T = \alpha (\nabla^2 T) \Delta t$$

Substituting the finite difference equation for $\nabla^2 T$ where the point under evaluation is not adjacent to the boundary:

$$\Delta T = T_{o; +1} - T_o = \alpha \Delta t \left[ \frac{T_1 - 2T_o + T_3}{2} + \frac{T_2 - 2T_o + T_4}{2} + \frac{1}{x} \frac{T_3 - T_1}{\Delta} \right] \tag{5}$$

$$T_{o, +1} = \alpha \Delta t \left[ \frac{T_1 + T_2 + T_3 + T_4}{2} + \frac{T_3 - T_1}{x \Delta} \right] + T_o \left(1 - \frac{4\alpha \Delta t}{\Delta^2}\right) \tag{6}$$

The term $\frac{\Delta^2}{\alpha \Delta t}$ imposes a restriction upon the grid size and time increment such that:

$$\frac{\Delta^2}{\alpha \Delta t} = M \geq 4$$

This factor is called the modulus, M, and if its value is less than 4 this leads to an unstable condition. A nonrigorous illustration will show why this is so. Suppose that $T_1$, $T_2$, $T_3$, and $T_4$ are equal and cooler than $T_o$. Equation (6) reduces to:

$$T_{o, +1} = \frac{4T_1 \alpha \Delta t}{\Delta^2} + T_o \left(1 - \frac{4 \alpha \Delta t}{\Delta^2}\right)$$

$$= \frac{4 \alpha \Delta t}{\Delta^2} (T_1 - T_o) + T_o$$

$$= \frac{4}{M} (T_1 - T_o) + T_o$$

If:

$$M > 4 \qquad T_{o,+1} > T_1$$

$$M = 4 \qquad T_{o,+1} = T_1$$

$$M < 4 \qquad T_{o,+1} < T_1$$

The condition $M < 4$ predicts that $T_o$ has cooled below its surroundings, or, in other words, energy has flowed "uphill". One would imtuitively guess that $T_o$ would approach $T_1$ at steady state. When $M = 4$ the system is conditionally stable, and when $M > 4$ the system is stable. Thus, once a $\Delta$ is chosen the range of $\Delta t$ is fixed. The most accurate results for finite difference techniques is obtained for small $\Delta$'s. However, $\Delta t$ must be very small to maintain stability, and the steady state is approached slowly. If one desires to obtain the solution more quickly, he must increase $\Delta t$, and, at the same time $\Delta$, thus losing grid accuracy. If a boundary is superimposed on the grid such that for points adjacent to that boundary, $P_3$ and $P_4$ are less than 1.0, the modulus is different than than calculated for the points on the interior. Here $\Delta$ is smaller, thus, $\alpha \Delta t$ must be decreased to maintain stability increasing computation time on the computer to reach steady state. For instance, in the whisker analysis, it was necessary to adjust $\alpha \Delta t$ such that $M = 4$ at the points adjacent to the edge, but for interior points the same $\alpha \Delta t$ gave $M = 20$ since the effective grid size changed.

The equation:

$$T_{j,+1} = T_j + \alpha(\nabla^2 T) \Delta t$$

Where: $\nabla^2 T$ = the sum of equations (1), (2), and (4),can

calculate the new temperature for points interior to the boundary provided proper values of $P_1$, $P_2$, $P_3$ and $P_4$ are used. However, for points on the boundary the image method is convenient to use (Ref. 14).

The image technique involves overlaying an imaginary grid line perpendicular to the point under consideration.

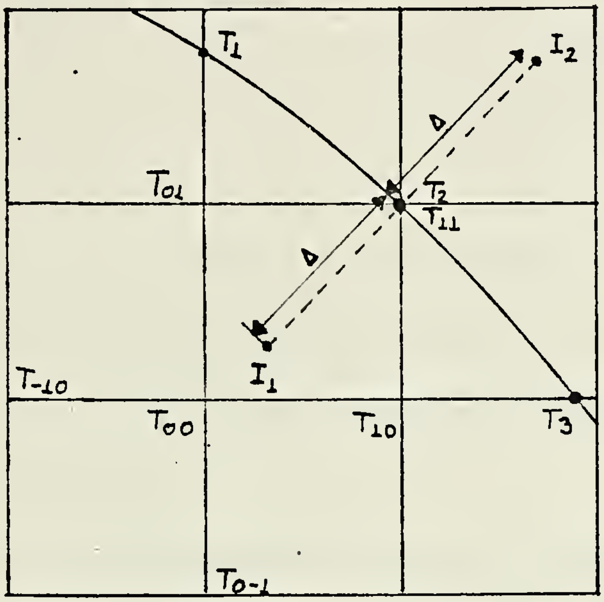



Fig. 12

Image point technique.

One is able to simulate the desired flux across the boundary by working with image temperatures $I_1$ and $I_2$. $I_1$ is the actual temperature at a distance one $\Delta$ inside the whisker normal to the point under consideration $T_2$. The value of $I_1$ can be found by interpolating between temperatures which are on grid points. For the above situation these temperatures would be $T_{00}$, $T_{01}$, $T_{10}$, $T_{0-1}$, $T_{-10}$, and $T_{11}$, and the method used for interpolation will be shown later.

$I_2$ is an imaginary temperature whose value is manipulated to

obtain the desired flux. For example, an insulated boundary is one through which heat does not flow. Therefore, the temperature gradient $\frac{\partial T}{\partial x}$ is 0 where x is understood to be the direction normal to the surface. In difference equation form this is:

$$\frac{\partial T}{\partial x} = \frac{I_2 - I_1}{2\Delta} = 0$$

Therefore:

$$I_2 = I_1$$

To calculate $T_{2,+1}$, equation (6) must be used. This assumes the boundary is linear over the interval from point 1 to point 3. The four temperatures $T_1$, $T_3$, $I_2$ and $I_1$ and their corresponding values of $P_1$, $P_2$, $P_3$, and $P_4$ would be used.

Interpolation to find $I_2$ involves many steps, the first of which is determining the slope at point 2. The method of calculation assumes a quadratic function describing the positions of points 1, 2, and 3, where the coordinates of these three points are:

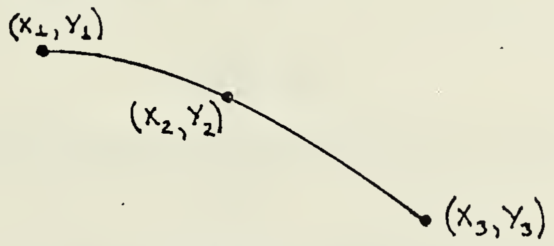



Fig. 13
Points used in approximation of slope

The function can be linearized about $(x_2, y_2)$ by Taylor series.

$$y_1 = y_2 + \left.\frac{dy}{dx}\right|_2 (x_1 - x_2) + \frac{1}{2} \left.\frac{d^2y}{dx^2}\right|_2 (x_1 - x_2)^2 + \ldots$$

$$y_3 = y_2 + \frac{dy}{dx}\bigg|_2 (x_3 - x_2) + \frac{1}{2}\frac{d^2y}{dx^2}\bigg|_2 (x_3 - x_2)^2 + \dots$$

Truncating after the third term and solving for $\frac{dy}{dx}$ evaluated at point 2:

$$\frac{dy}{dx}_2 = \frac{1}{x_3 - x_2 - \dfrac{(x_3 - x_2)^2}{(x_1 - x_2)}} \left[ y_3 - y_2 + \frac{(x_3 - x_2)^2}{(x_1 - x_2)^2}(y_2 - y_1) \right] \quad (7)$$

It is necessary to use the above slope to calculate the physical position of $I_1$ in relation to $T_{00}$ in order to imterpolate a value for $I_1$.

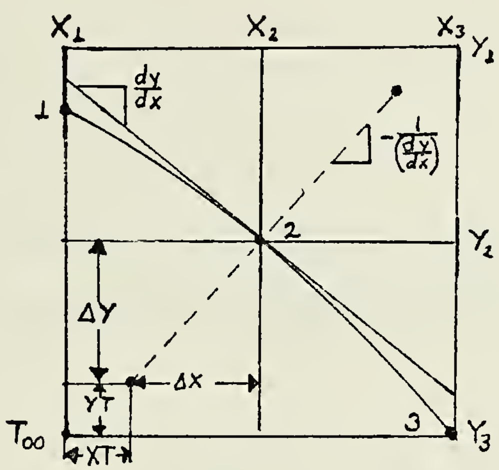



Fig. 14

Determining position of image points.

From Fig. 14 one can derive the distances XT and YT which are used later in the interpolation process.

$$\Delta x^2 + \Delta y^2 = \Delta^2$$

$$\Delta y = \Delta x \left(\frac{-1}{\frac{dx}{dx}}\right)^2$$

Substituting:

$$\Delta x^2 + \Delta x^2 \left(\frac{1}{\frac{dy}{dx}}\right)^2 = \Delta^2$$

$$\Delta x = \Delta \cdot \left(\frac{1}{1 + \frac{1}{\left(\frac{dy}{dx}\right)^2}}\right)^{\frac{1}{2}} \tag{8}$$

By a similar derivation:

$$y = \Delta \cdot \left(\frac{1}{1 + \left(\frac{dy}{dx}\right)^2}\right)^{\frac{1}{2}}$$

Then:

$$xT = x_2 - \Delta x - x_1$$

$$yT = y_2 - \Delta y - y_1$$

$I_1$ was determined by using a six-point interpolation formula in the following manner: (utilizing the points shown in Fig. 15)

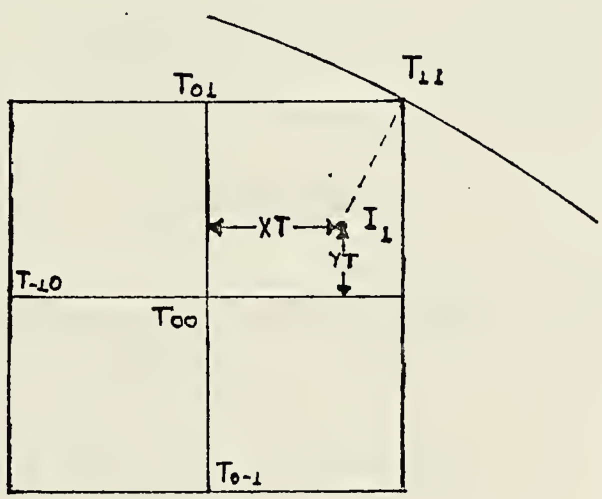



Fig. 15
Points used for six point interpolation.

A second order, two-dimensional Taylor series yields:

$$I_1 = T_{00} + (T_x)_{\substack{x=0\\y=0}} (xT) + \tfrac{1}{2} (T_{xx})_{\substack{x=0\\y=0}} (xT)^2 + (T_y)_{\substack{x=0\\y=0}} (yT) \tag{9}$$

$$+ \tfrac{1}{2} (T_{yy})_{\substack{x=0\\y=0}} (yT)^2 + \tfrac{1}{2} (T_{xy})_{\substack{x=0\\y=0}} (xT)(yT)$$

Where:

$$(T_{xx})_{\substack{x=0\\y=0}} = \frac{\partial^2 T}{\partial x^2} \text{ evaluated at } T_{00}.$$

$$(T_y)_{\substack{x=0\\y=0}} = \frac{\partial T}{\partial y} \text{ evaluated at } T_{00}.$$

, and so forth.

Referring to the basic finite difference expressions for first and second partials one can see them in terms of the unit grid size:

$$(T_x)_{\substack{x=0\\y=0}} = \frac{T_{10} - T_{-10}}{2}$$

$$(T_{xx})_{\substack{x=0\\y=0}} = T_{10} - 2T_{00} + T_{-10}$$

$$(T_y)_{\substack{x=0\\y=0}} = \frac{T_{01} - T_{0-1}}{2}$$

$$(T_{yy})_{\substack{x=0\\y=0}} = T_{01} - 2\,T_{00} + T_{0-1}$$

An expression for $(T_{xy})_{\substack{x=0\\y=0}}$ was formulated by solving expansions where temperatures are known:

$$T_{01} = T_0 + (Ty)_{\substack{x=0\\y=0}} + \tfrac{1}{2} (Tyy)_{\substack{x=0\\y=0}}$$

$$T_{11} = T_0 + (T_x)_{\substack{x=0\\y=0}} + \tfrac{1}{2} (T_{xx})_{\substack{x=0\\y=0}} + (T_y)_{\substack{x=0\\y=0}} + \tfrac{1}{2}(T_{yy})_{\substack{x=0\\y=0}}$$

$$+ \tfrac{1}{2} (Txy)_{\substack{x=0\\y=0}}$$

Solving simultaneously:

$$(T_{xy})_{\substack{x=0\\y=0}} = 2\left(T_{11} - T_{01} - (T_x)_{\substack{x=0\\y=0}} - \tfrac{1}{2}(T_{xx})_{\substack{x=0\\y=0}}\right)$$

Substituting $T_x$ and $T_{xy}$:

$$(T_{xy})_{\substack{x=0\\y=0}} = 2T_{11} - 2T_{01} - 2T_{10} + 2T_{00}$$

Thus, $I_1$ may now be calculated by substituting the proper values of xT, yT and the above difference equations into equation (9).

## C. COMPUTED RESPONSES OF THE WHISKER TO BOUNDARY CONDITIONS

When a whisker is in the growth environment there are several boundary conditions to be met at the whisker surface. From the interior heat is transferred to the surface by conduction.

$$q = -kA \frac{\partial T}{\partial x}$$

The heat flow leaving the surface is governed by several effects. Convection and radiation depend upon the temperature difference between the surface and atmosphere. Both factors are complicated by the film of adsorbed gas or liquid present on the boundary as well as the flow of hydrogen past the surface. Thus, the proportionality constants for each effect would be very difficult to determine experimentally.

However, a few predictions may be made from some simple calculations. It has previously been shown (pg. 56) that the flow of heat for

an iron whisker growing by reduction of $FeCl_2$ at $100\mu$/sec is approximately -35 cal/sec due to the endothermic reaction. Since convection as well as radiation depend upon temperature differentials, an initial approximation was made where the chemical reaction was the only factor taken into consideration.

An additional factor that is present in the cold tip theory of whisker growth is the heat imparted by the diffusion up the sides of the whisker by the liquid halide. However, this was not treated here due to the complexity of this particular type of heat transfer.

Two types of boundary conditions were imparted to the surface and the responses studied. First, as a control to see the type of heat flow within the geometry of a whisker, the surface was insulated. The calculations used to study this involved giving the surface a thermal shock at time = 0. Then the whisker responded by a heat flow due only to conduction from the base. This response is shown by the isotherms of the whisker drawn on the next few pages.

A word of explanation concerning the isotherms is appropriate at this time. The figures are scaled to contour the temperature arrays from a computer, consequently, the horizontal scale is different from that of the vertical. Temperatures of the isotherms are on the right side with the value in the upper right hand corner indicating the temperature at the tip. An isotherm of constant value is drawn across the base to indicate the the heat source. The isotherms resembling steps are due to the fact that only three significant figures were stored in the arrays. For example, a temperature of 29.95°C is stored as 30.00°C.

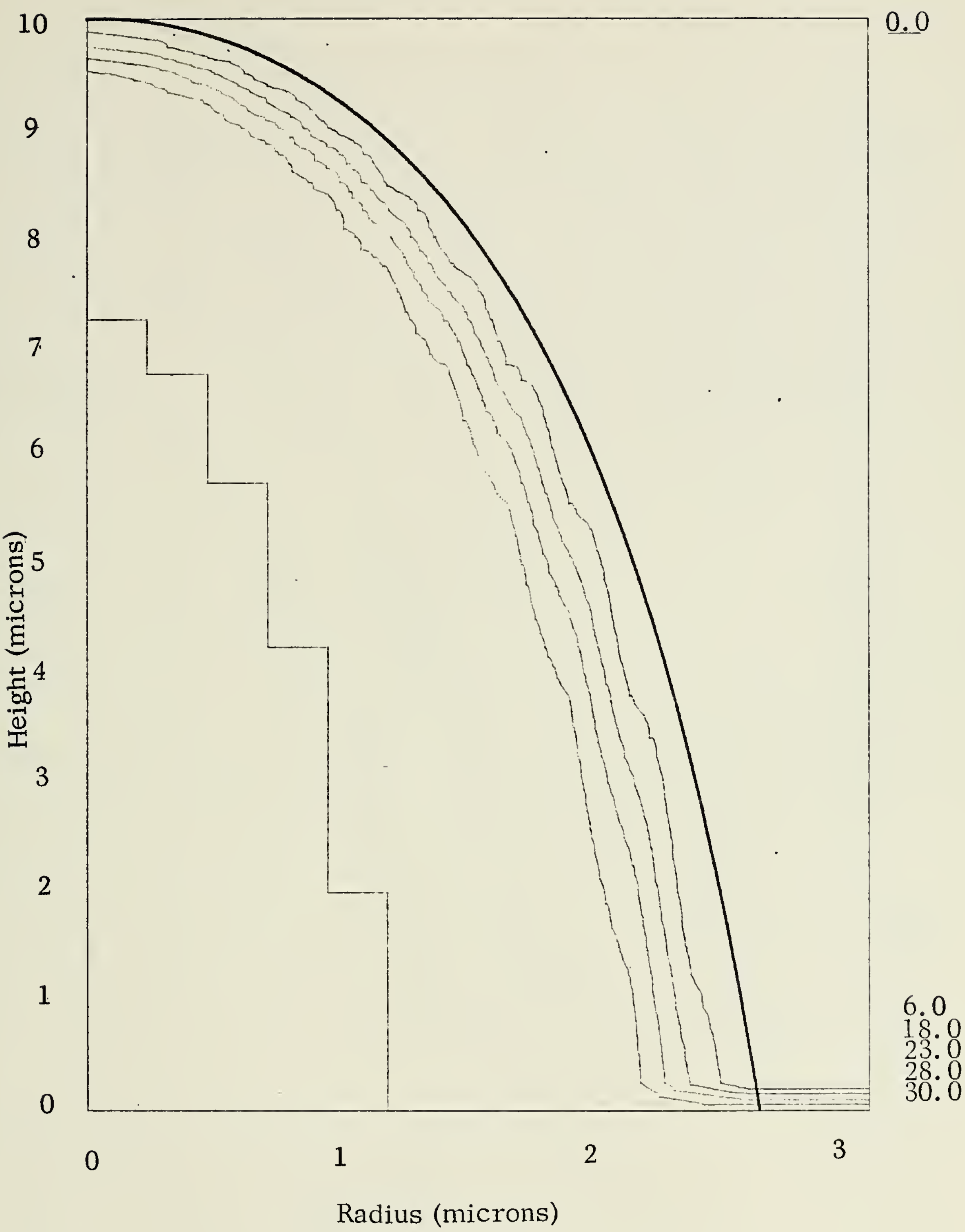



Fig. 16

Initial condition of pulsed whisker

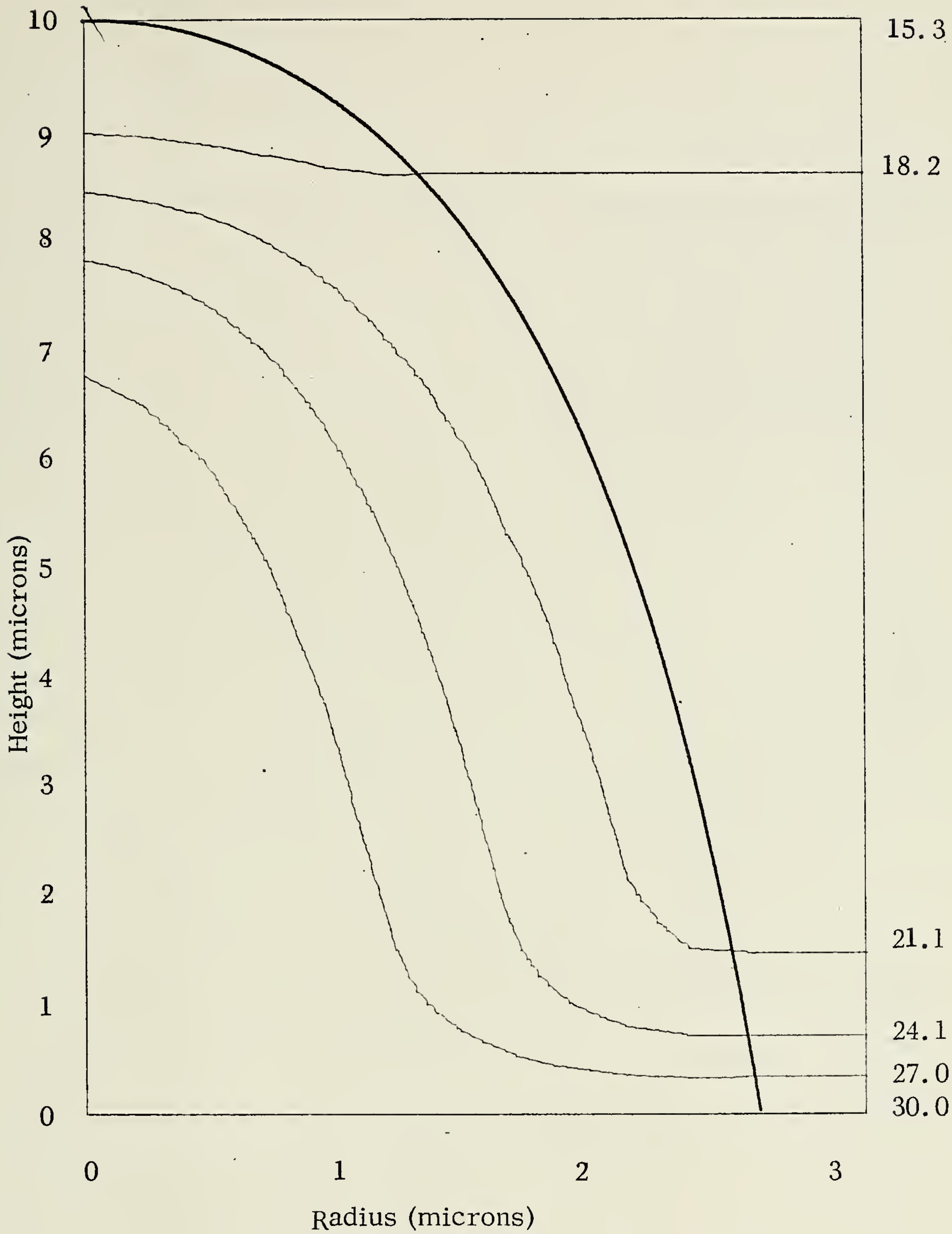



Fig. 17

Isotherms after 100 iterations.

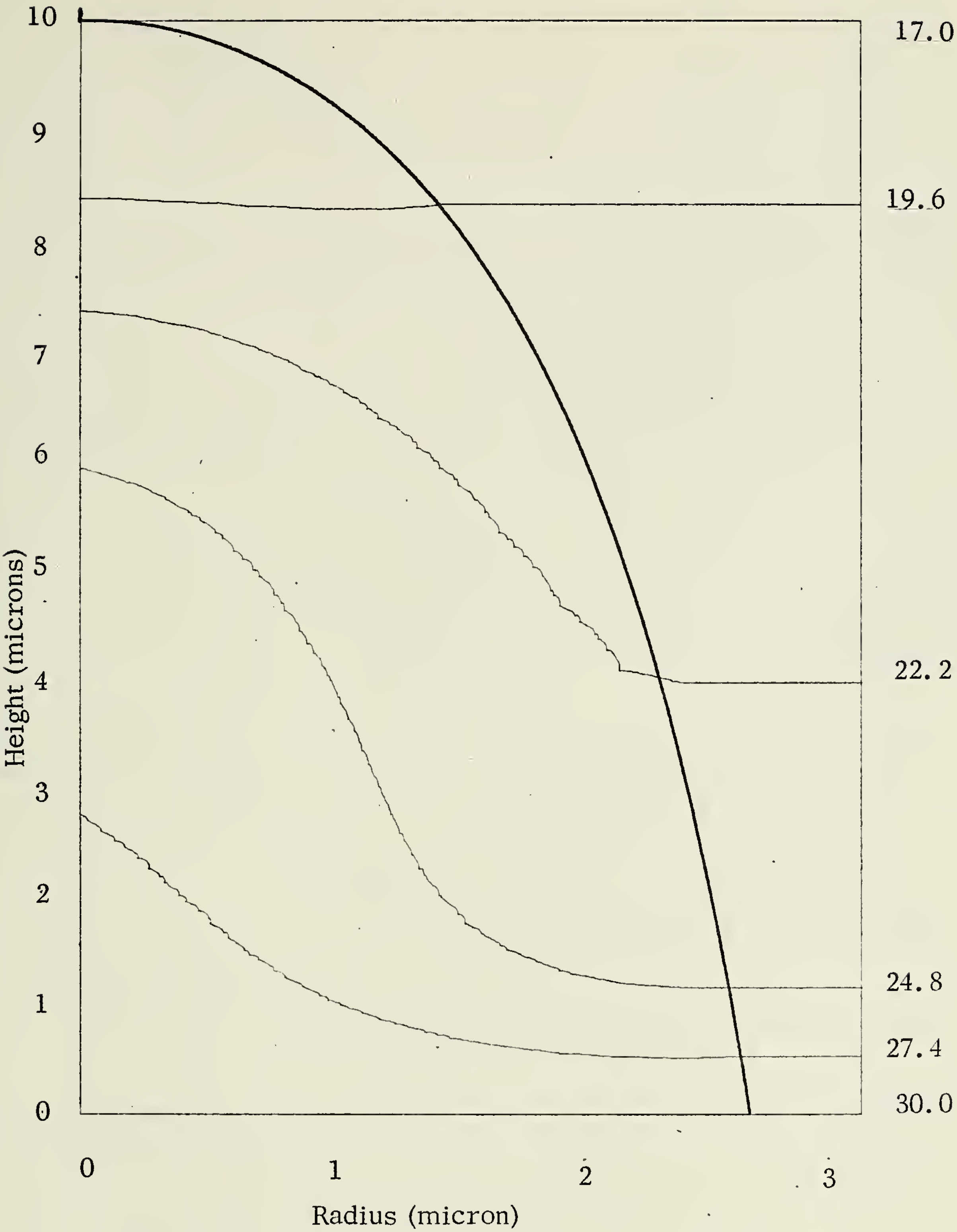



Fig. 18

Isotherms after 200 iterations.

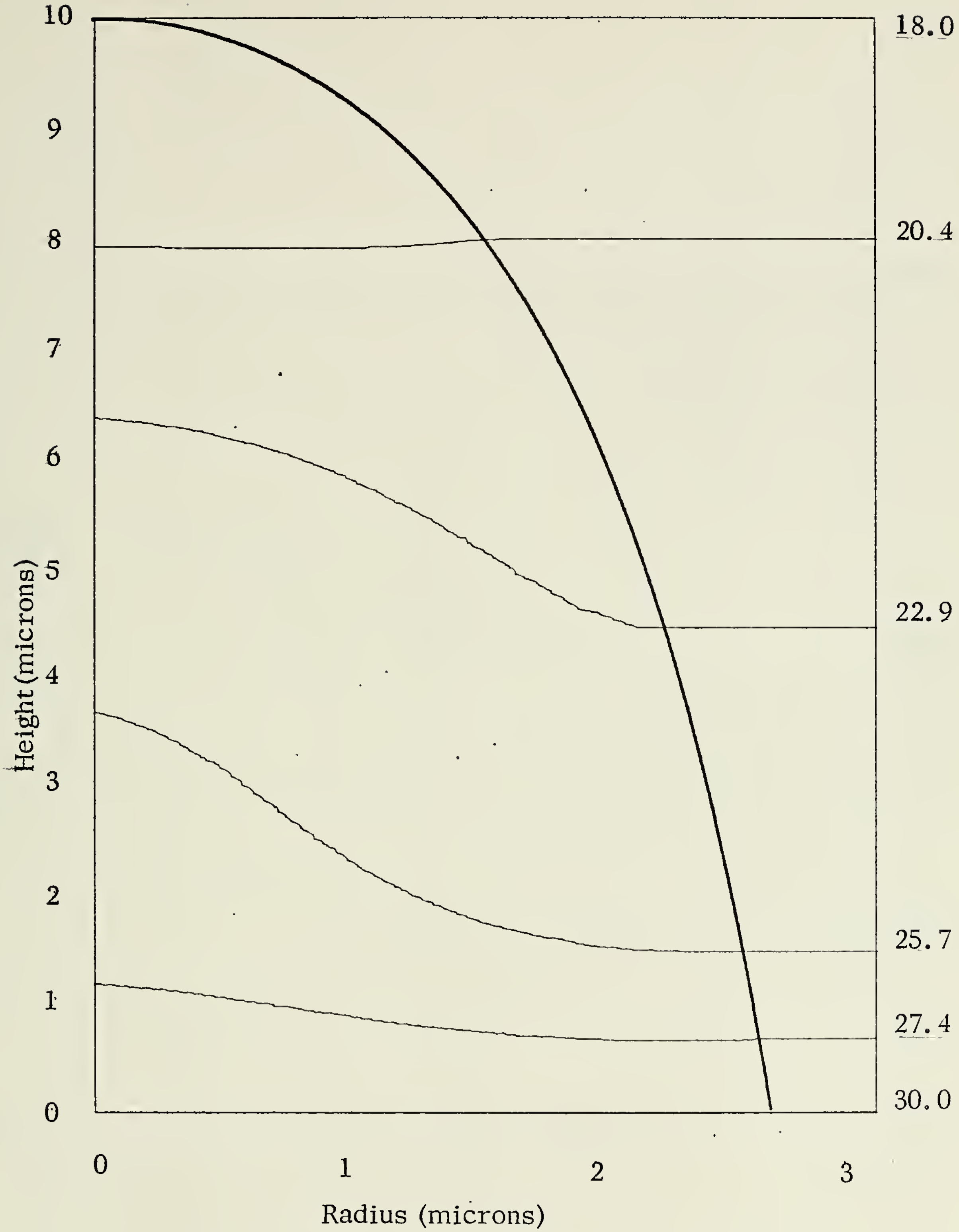



Fig. 19

Isotherms after 300 iterations.

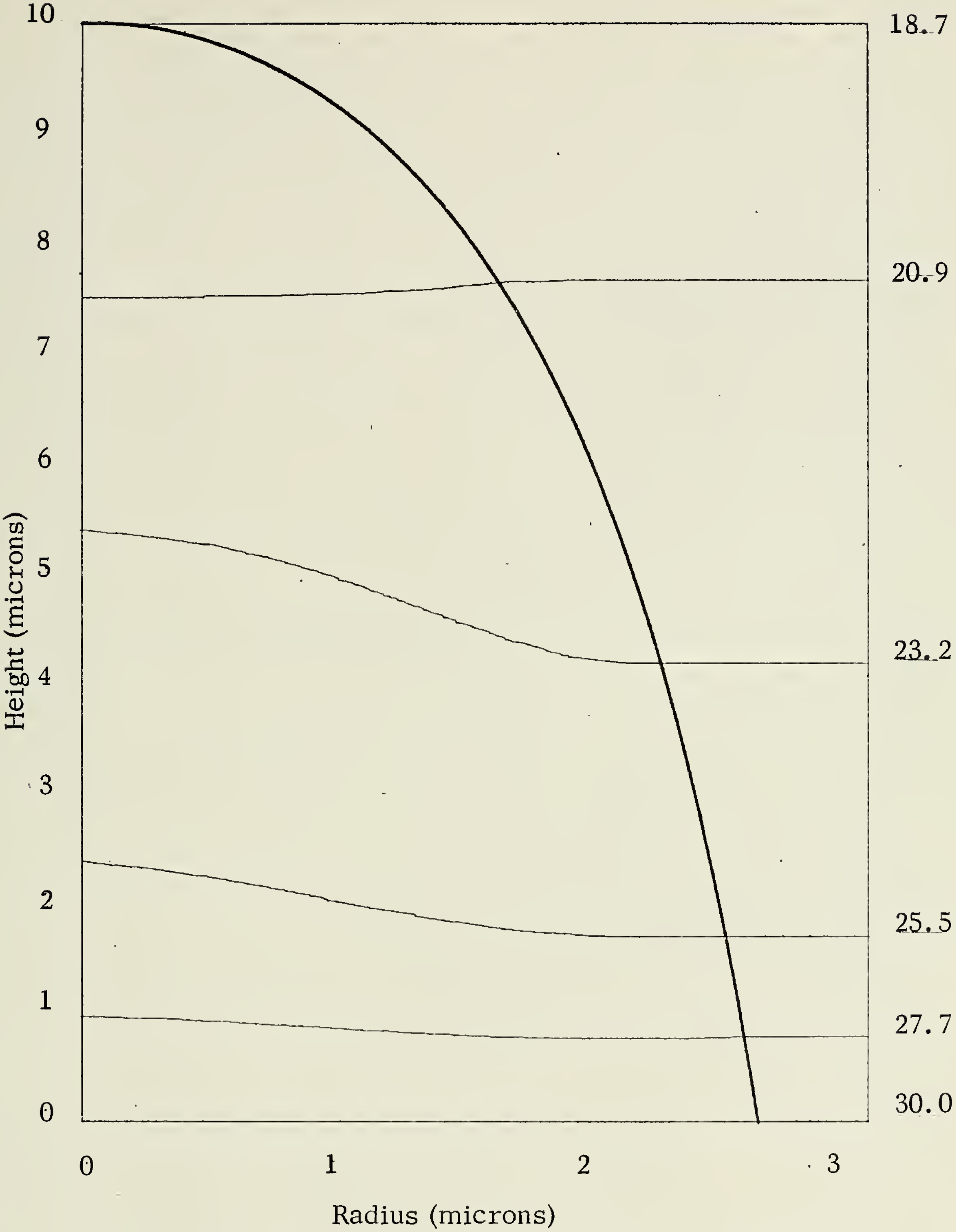



Fig. 20

Isotherms after 400 iterations.

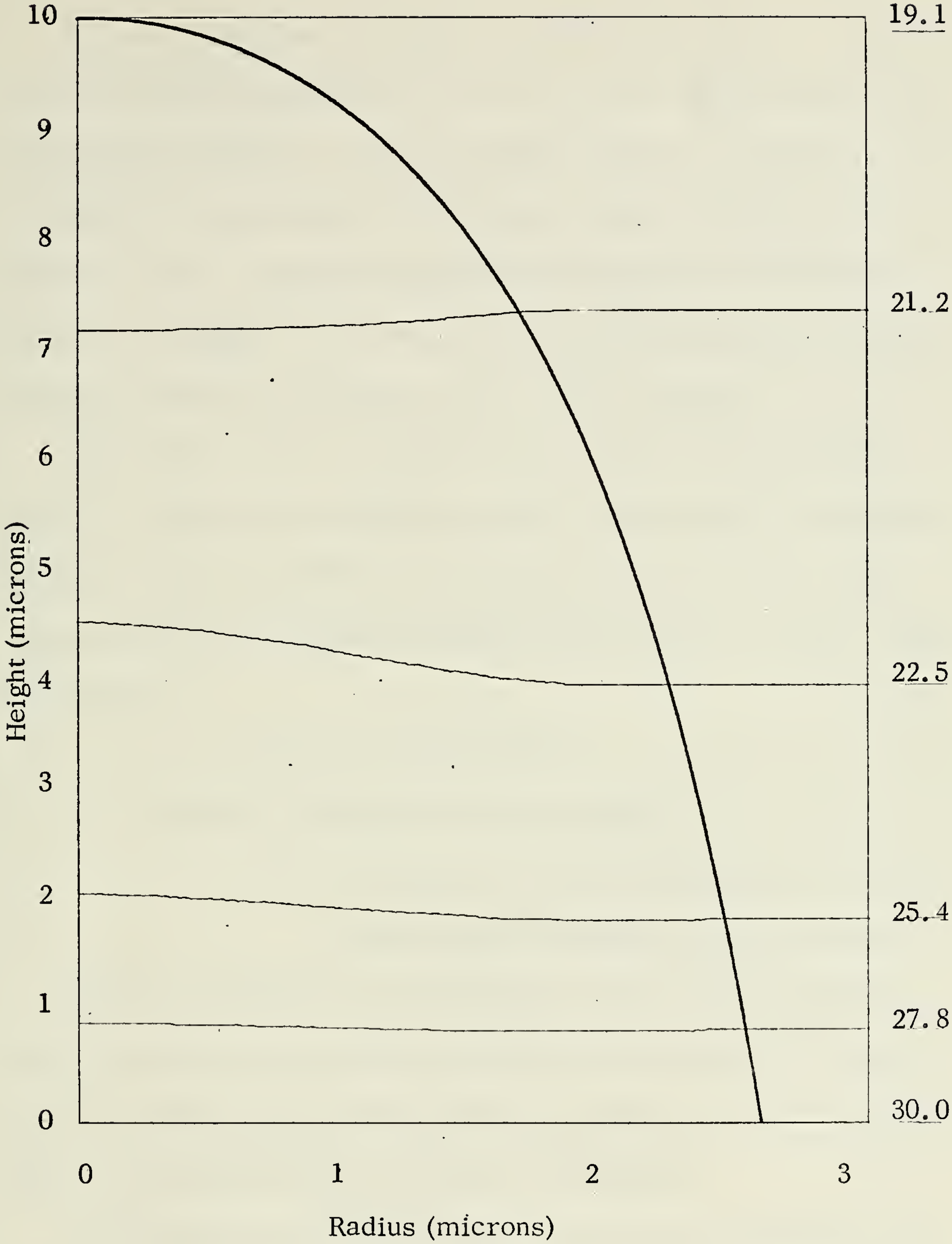



Fig. 21

Isotherms after 500 iterations.

The time shown was calculated from the interval $\alpha \Delta t$. To understand this refer to equation (5): here $\alpha \Delta t$ was a quantity used to multiply the finite difference. In the computer analysis, a value for $\alpha \Delta t$ of 0.003 was determined to be the largest number allowing a stable solution, that is, a modulus approximately equal to 4. $\alpha$ for iron at $1000^{\circ}K$ is $0.04 \frac{cm^2}{sec}$ or $4 \times 10^6 \mu^2/sec$. Since $\alpha \Delta t$ equals 0.003 the true time interval per iteration is $0.75 \times 10^{-9}$ seconds.

The thermal shock was applied at the surface in the following manner: a temperature difference of $30^{\circ}C$ was assumed to take place between the base and surface. The temperatures at all other points were calculated as a function of their distance from the surface. This function was:

$$T = 30 \cdot (1 - \exp(-B \cdot D^2))$$

Where: D = Distance from the surface.

B = An arbitrary number describing the attenuation of the shock with distance into the interior.

From an examination of the positions of the isotherms with time one can see that the tip is the coolest point on the whisker. It can be seen after 500 iterations the temperature is dependent almost exclusively upon the distance from the base as is expected.

The next series of isotherms was drawn from the treatment of the chemical reaction at the surface. It was assumed that the whisker and atmosphere were at the same temperature and the surface was covered uniformly by the necessary halide for the growth mechanism. At

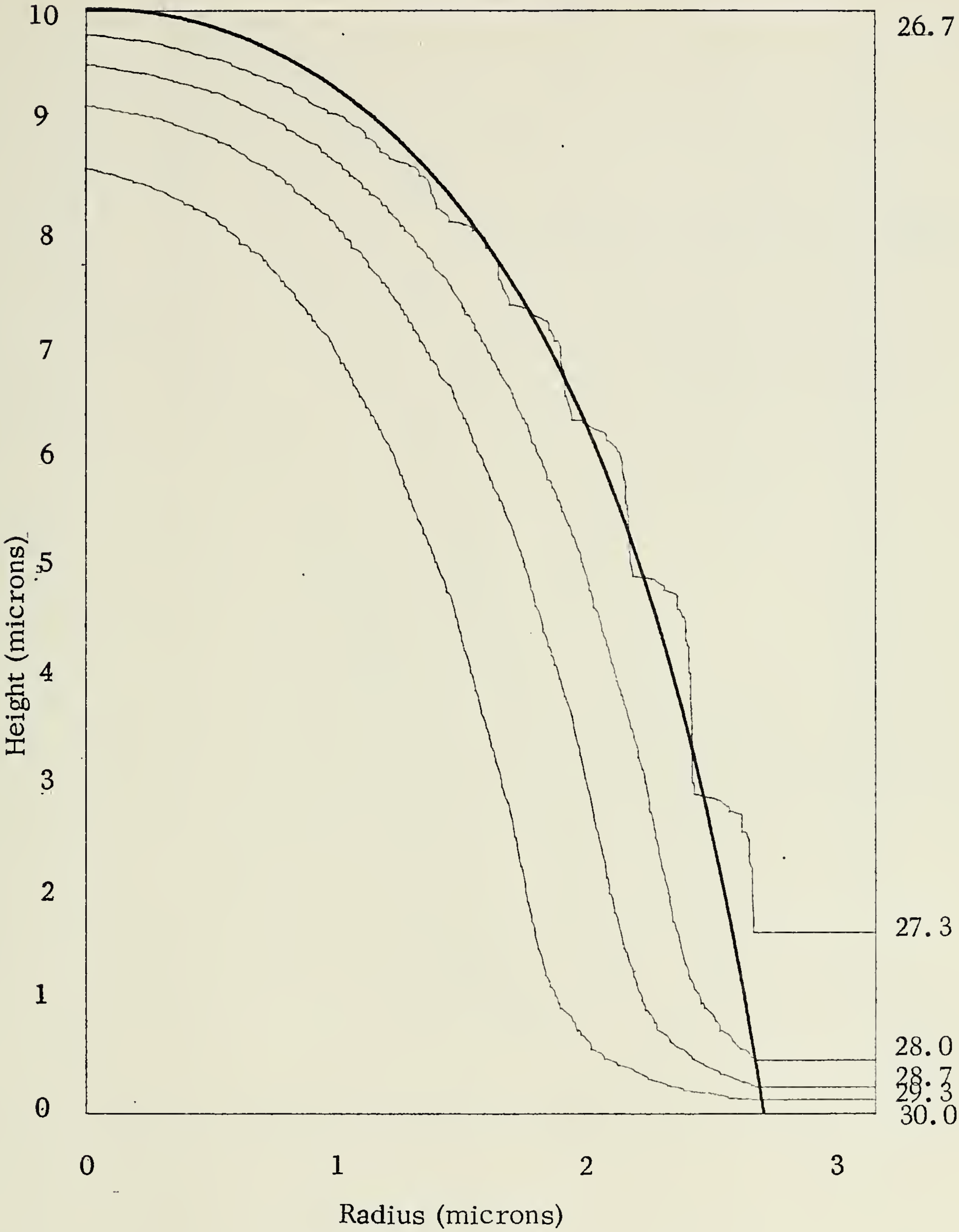



Fig. 22

Whisker isotherms after 100 iterations.

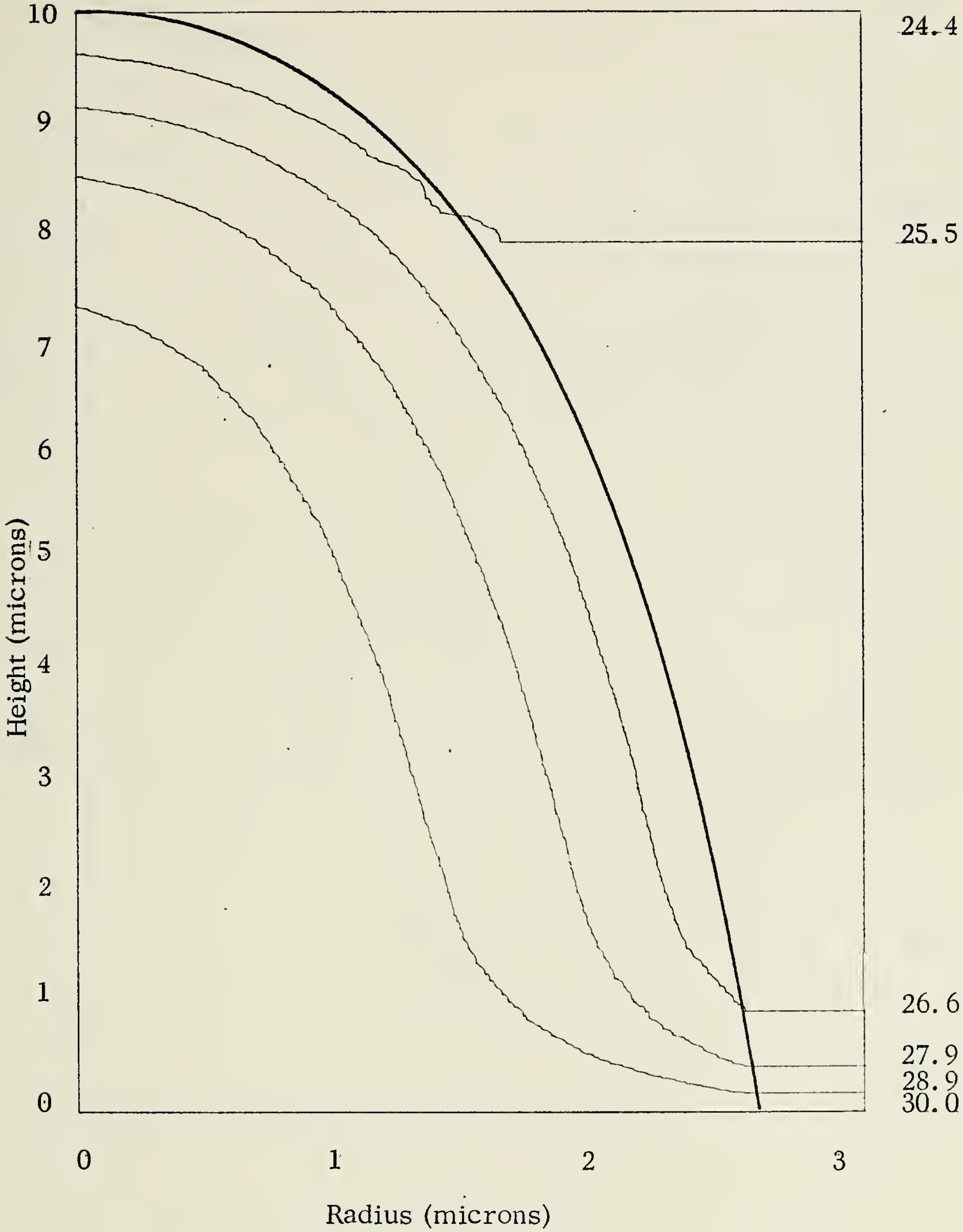



Fig. 23

Whisker isotherms after 200 iterations.

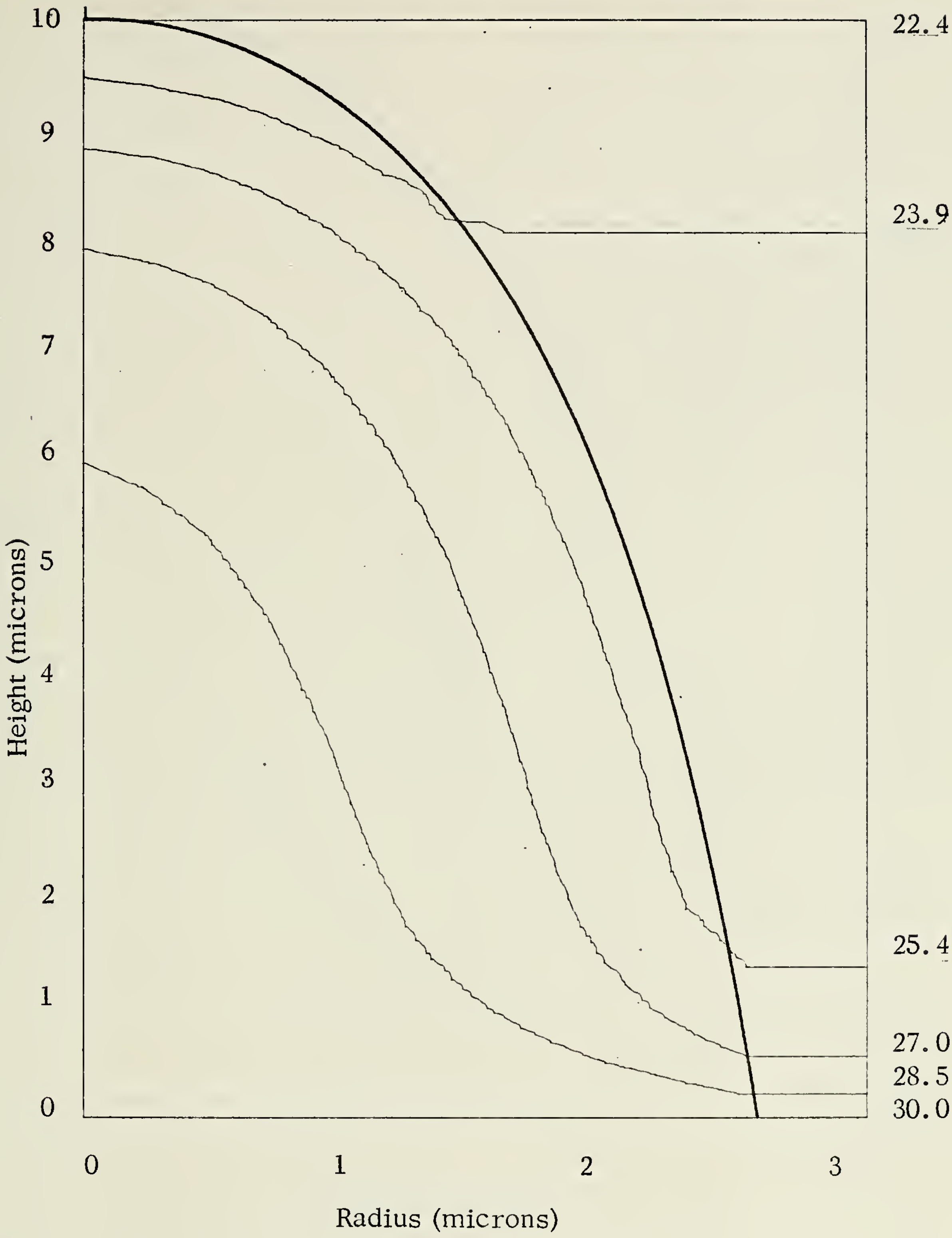



Fig. 24

Whisker isotherms after 300 iterations.

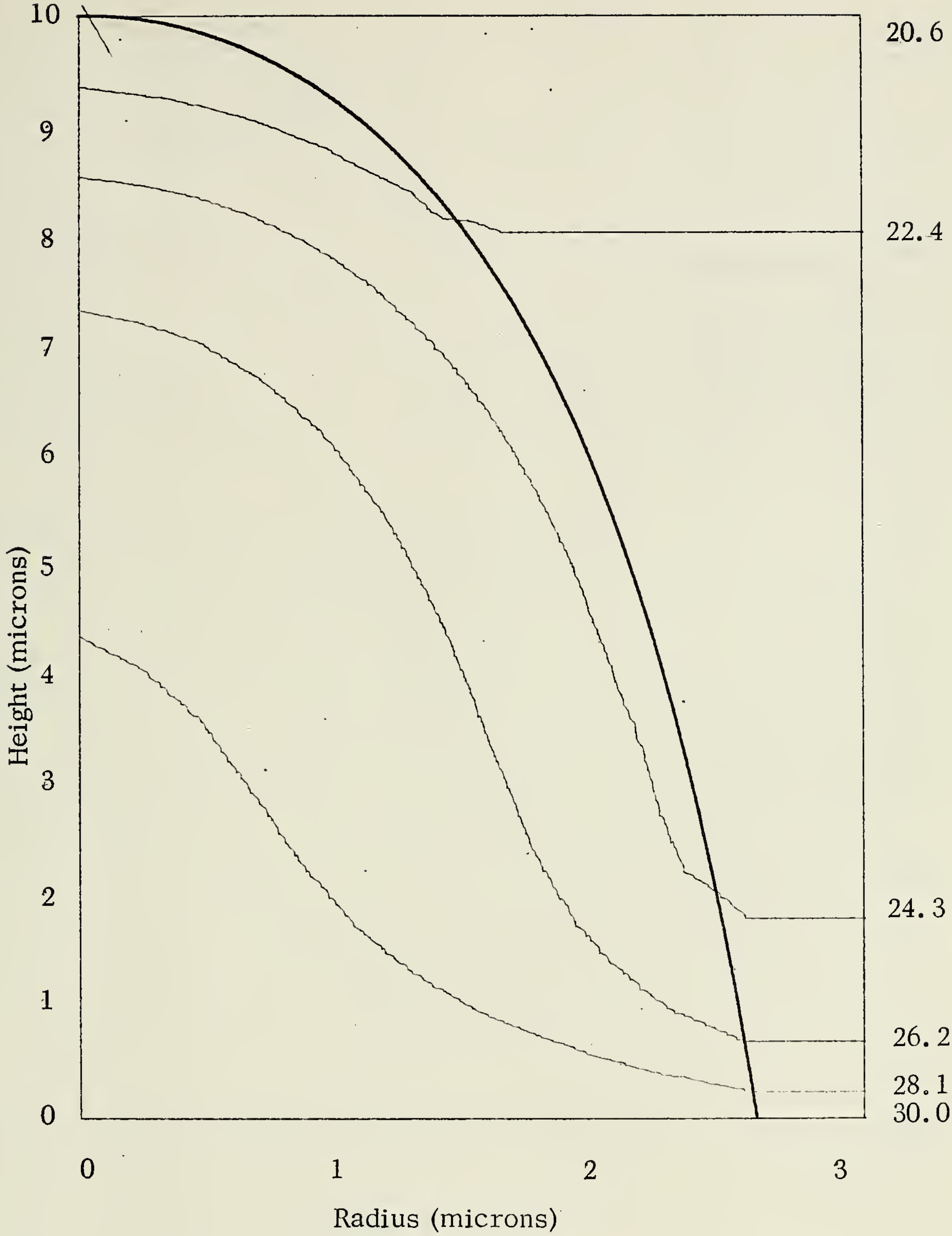



Fig. 25

Whisker isotherms after 400 iterations

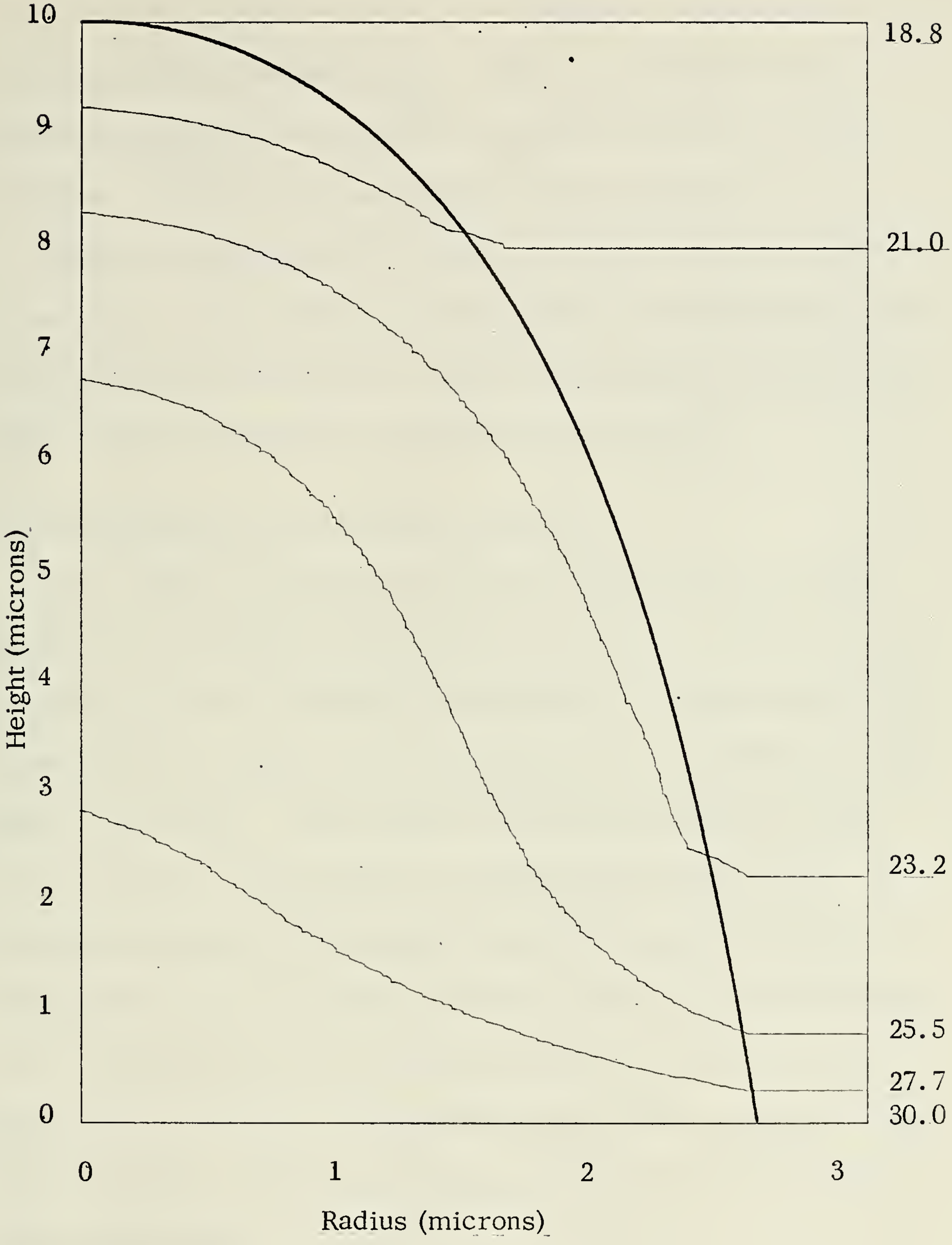



Fig. 26

Whisker isotherms after 500 iterations.

time = 0 the reaction was started. The reaction was treated as if it occured uniformly over the surface. Also, it was assumed that it withdrew enough heat at all points to cool the surface by $0.1^{o}C$ per iteration. The surface was again assumed to be insulated.

From an examination of the series, one can see the tip is still the coldest point on the whisker. In comparison to the previous case where the endothermic reaction was not under consideration, one can see the entire whisker is gradually cooling instead of warming.

## D. SUGGESTIONS FOR FURTHER ANALYSIS

The computer modelling done to date on this problem has been limited in its consideration of $FeCl_2$ on the side of the whisker. One can see in the series of isotherms calculated with consideration of the chemical reaction (Figs. 22 - 26) temperatures are low adjacent to the sides of the whisker. This situation would be eliminated by taking into account heat transfer between the diffusing liquid and metal. At the base the liquid is at the temperature of the base. As it moves the temperatures inside the metal are lower than the base due to the cold tip. Consequently there is a temperature gradient present such that heat flows into the metal. Temperature of the metal increases and the liquid decreases. Thus, as the tip is approached the liquid has been cooled appreciably.

The second consideration is the kinetics of the rate of diffusion with distance from the base. Growth rate will decrease due to the

greater distance and hence longer time necessary to migrate to the tip. This is an area of study deserving extensive consideration and needs to be applied to the present model.

## V. SUMMARY

The work of this paper can be summarized as follows: the cold tip mechanism put forth could be the correct mechanism for the growth of metallic whiskers. At the least, an examination in this direction has shed new ideas on how to explain whisker growth phenomenon. It predicts the diffusion of the metal halide in the liquid state from thermodynamic considerations. What is needed to continue the theory is an extensive analysis of the diffusion of this liquid keeping the cold tip in consideration.

## APPENDIX A

### Computer Modeling

Due to the particular boundary under consideration, an extensive explanation of how the mathematics of section B were adapted to the computer is necessary. First it was necessary to make several basic assumptions about the system. The whisker was assumed to have the dimensions of 10 microns in length (L) at the stage of growth under observation. The physical boundary was described arbitrarily by the equation:

$$Y = L - (AX^2) / (r^2 - X^2)$$

Where:

Y = The vertical coordinate coincident with the longitudinal axis.

X = The radial distance from the center.

A = A dimensionless parameter which changes the desired curvature of the whisker. The larger the value of A the sharper the curvature.

r = The radius of the whisker at full growth.

Since it was decided that the whisker was perfectly round, the above equation described a parabolic cone. This symmetry simplified the problem, and thus it was only necessary to treat the points on one

side of the central axis. A unit grid size of 0.25 microns was laid over the whisker in order to apply finite difference techniques (Fig. 6). Several assumptions were then made for the environment of this whisker. The base was assumed to be resting upon a heat source, thus the base was kept at constant temperature. No attempt was made to account for the cooling of the atmosphere by the endothermic reaction, that is, it was considered insulated from the whisker surface. Thus, the temperature of the atmosphere was constant everywhere it contacted the metal surface. Also, the whisker boundary was not allowed to move as if it were growing. This greatly simplified the problem and confined the study of heat flow to just the curvature of the boundary and the cooling due to the chemical reaction.

First it was necessary to formulate a two dimensional array of temperatures called T(I, J). I corresponded to the element in the x dimension and J in the y dimension. The grid size of 0.25 microns was called $\Delta$ in the derivations for the difference equations. Here it was given the name DEL. Thus, the physical position (X, Y) of the (I, J) element which was interior to the surface element was:

$$x = (I - 1) \cdot DEL$$

$$y = (J - 1) \cdot DEL$$

Complications arose when it was desired to represent the surface points. The convention used can more easily be understood from the following diagram:

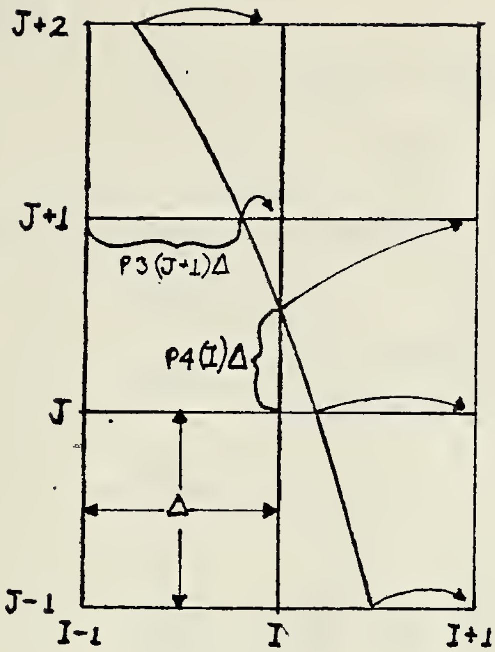



Fig. 27
Assignment of temperatures to grid points

The above diagram shows the two situations that arose. Temperatures were assigned to points where the boundary intersected the grid. If the boundary intersected the horizontal grid line of value J then this temperature was stored in the (I + 1, J) element. If the boundary intersected the vertical grid line I shown, its value was stored in the (I + 1, J + 1) element.

To determine how the boundary intersected the grid a test for each point and its relation to the boundary was formulated. The vertical distance from a point to the surface was called YPY.

$$YPY = YP - Y$$

Where:

$$YP = L - (AX^2) / (r^2 - X^2)$$

$$Y = (J - 1) \cdot DEL$$

The horizontal distance to the surface was XPX.

$$XPX = XP - X$$

$$XP = \left[ \frac{(L - Y)\, r^2}{(A + L - Y)} \right]^{\frac{1}{2}}$$

$$X = (I - 1) \cdot DEL$$

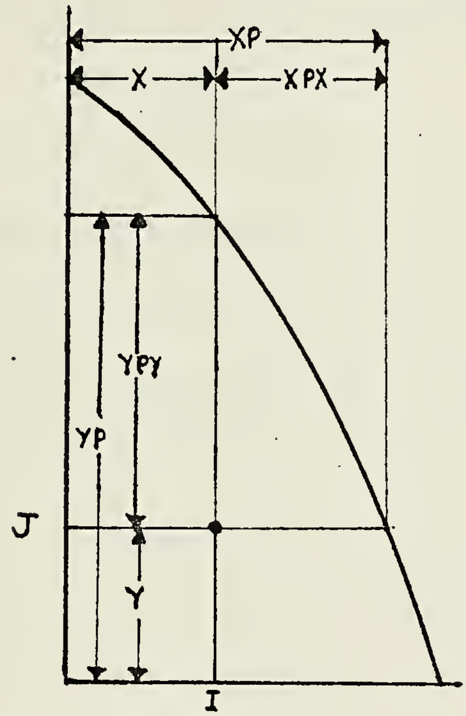



Fig. 28
Testing element (I, J)'s proximity to surface

If XPX was less than DEL the boundary intersected the horizontal grid line between the I and I + 1 element. Consequently the surface temperature at this intersection was stored in the (I + 1, J) element. Similarly, if YPY was less than DEL, the temperature of the point

represented at the intersection of the vertical grid line and boundary was stored in the (I + 1, J + 1) element.

If one recalls the difference equations (1), (2), and (4), it can be seen that for all points not adjacent to the surface the fractions $P_1$, $P_2$, $P_3$, and $P_4$ were such that they were all equal to 1.0. However, for the adjacent points, $P_3$ and $P_4$ became fractions while $P_1$ and $P_2$ remained 1.0. When a point was tested in the program and found that either or both XPX and YPY were less than DEL, $P_3$ and $P_4$ were calculated and stored in the one dimensional arrays $P_3(J)$ and $P_4(I)$ respectively by:

$$P_3(J) = XPX / DEL$$

$$P_4(I) = YPY / DEL$$

These arrays were one dimensional since $P_3(J)$ and $P_4(I)$ were unique for each horizonal and vertical grid line as seen in Fig. 8.

At the same time, it was desirable for later logic statements to assign a number to the various points in the array. A new two dimensional array IN was formulated such that:

IN(I, J) = 1 for all points interior to the surface.

IN(I, J) = 2 for all points on the surface.

IN(I, J) = 0 for all points outside the whisker.

The computer logic necessary for this testing and assigning technique can be seen under subroutine ASSIGN in the appendix.

The next phase in adapting the whisker to the computer model was to assign the values $T_1$, $T_2$, $T_3$, and $T_4$ to evaluate $T_{o,+1}$ by equation (6). The general case for points inside the boundary was:

$$ZO = T(I, J)$$

$$Z1 = T(I-1, J)$$

$$Z2 = T(I, J-1)$$

$$Z3 = T(I+1, J)$$

$$Z4 = T(I, J+1)$$

Where:

ZO = TO, Z1 = T1; and so fourth.

However, exceptions to the above case had to be made for several cases. If I=1, that is, if the x coordinate = 0, Z1= T(I+1, J) due to the symmetry of the whisker. Along the base, which was a heat source at a constant temperature called TINT, Z2 = TINT. For points directly below points where the boundary crossed the vertical grid lines Z4 = T(I + 1, J + 1), since the value of the temperature at the intersection was stored in the (I + 1, J +1) element. The computer logic for these steps is contained in subroutine TNEW.

Once the above values were assigned the change in temperature per unit time was calculated using equation (6). This change for every point interior to the surface was assigned to the two-dimensional array DELTAT. The logic for this operation is contained in subroutine DERIV.

Now that the change in temperature per unit time for interior points had been calculated it was necessary to treat the edge points. First it was necessary to assign X - Y coordinates to these surface points.

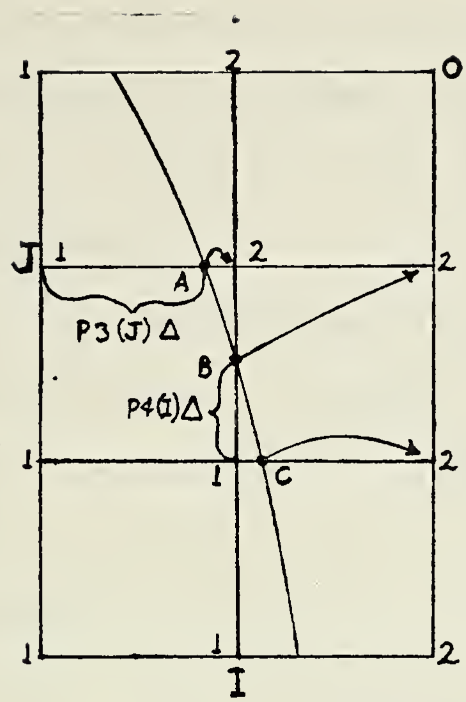



Fig. 29
Assignment of coordinates to surface points.

In the above diagram, one can see the usefulness of the IN array whose values are shown at the grid points. When a point was recognized to have a value of 2 its x coordinate was assigned:

$$x = (I-1 + P_3\ (J)\ ) \cdot \text{DEL}$$

$$y = (J-1) \cdot \text{DEL}$$

These assignments were valid for points like A and C. For points of type B:

$$x = (I-1) \cdot \text{DEL}$$

$$y = (J-2 + P_4\ (I-1)\ ) \cdot \text{DEL}$$

The next phase of the problem was to calculate the value of the

image point one DEL normal to the surface at the point under evaluation. First the slope of the function at that point was determined. This was done by evaluating equation (7). However, several different expressions were needed to find the three sets of coordinates $(x_1, y_1)$, $(x_2, y_2)$ and $(x_3, y_3)$. (See Fig. 30)

The expression for these coordinates were:

(a) $x_2 = (I-2+P_3(J)) \cdot DEL$ $\quad y_2 = (J-1) \cdot DEL$

$x_1 = (I-2+P_3(J+1)) \cdot DEL$ $\quad y_1 = J \cdot DEL$

$x_3 = (I-2+P_3(J-1)) \cdot DEL$ $\quad y_3 = (J-2) \cdot DEL$

(b) Same as (a) except:

$x_1 = (I-2) \cdot DEL$ $\quad y_1 = (J-1+P_4(I-1)) \cdot DEL$

(c) $x_2 = (I-2) \cdot DEL$ $\quad y_2 = (J-2+P_4(I-1)) \cdot DEL$

$x_1 = (I-3+P_3(J-1)) \cdot DEL$ $\quad y_1 = (J-1) \cdot DEL$

$x_3 = (I-2+P_3(J-1)) \cdot DEL$ $\quad y_3 = (J-2) \cdot DEL$

(d) Same as (a) except:

$x_3 = (I-1) \cdot DEL$ $\quad y_3 = (J-2+P_4(I)) \cdot DEL$

(e) $x_2 = (I-2+P_3(J)) \cdot DEL$ $\quad y_2 = (J-1) \cdot DEL$

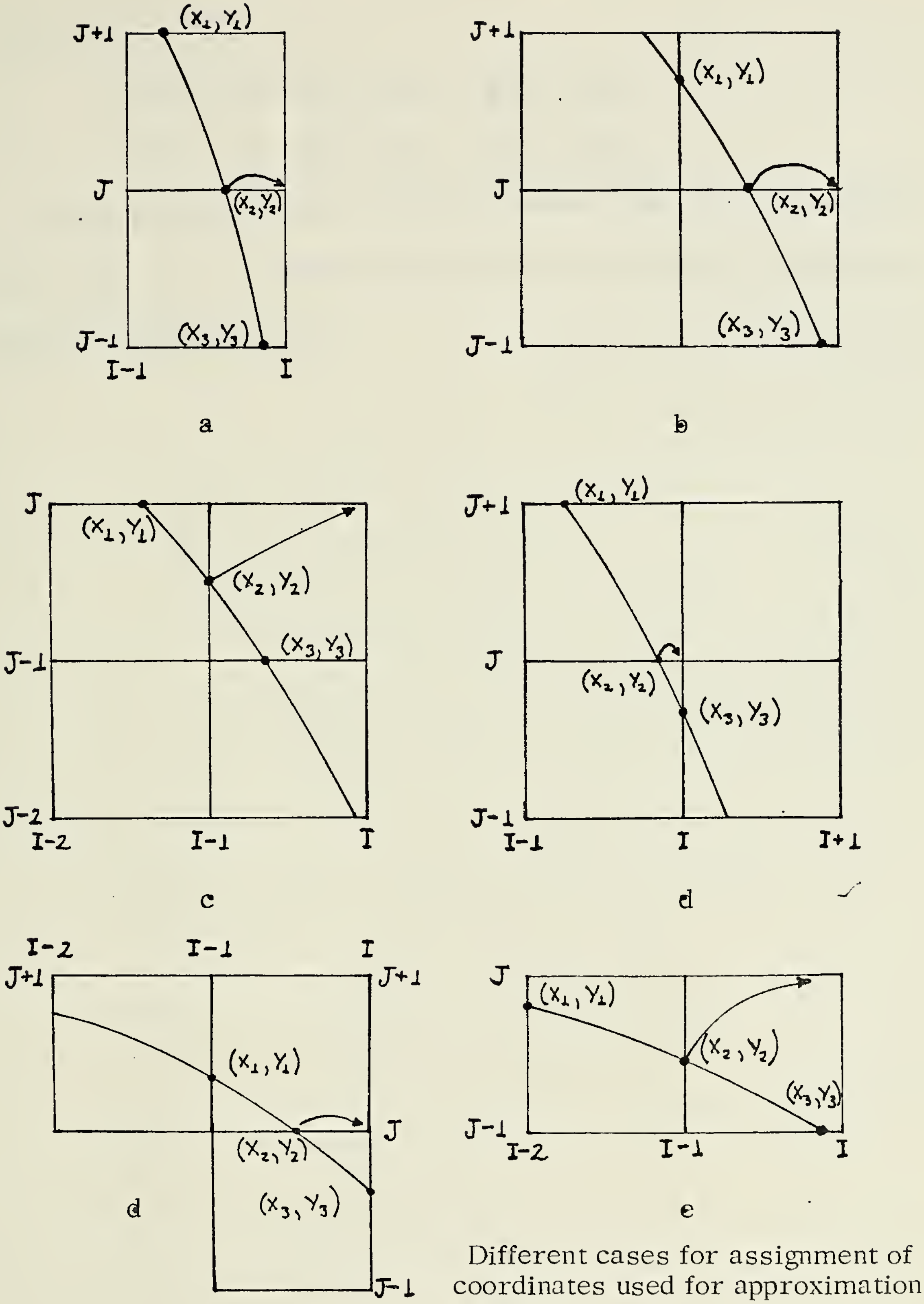
$x_1 = (I-2) \cdot DEL$ $\quad y_1 = (J-1+P_4(I-1)) \cdot DEL$

$x_3 = (I-1) \cdot DEL$ $\quad y_3 = (J-2+P_4(I)) \cdot DEL$

(f) Same as (c) except:

$x_1 = (I-3) \cdot DEL$ $\quad y_1 = (J-2+P_4(I-2)) \cdot DEL$

The final values left to calculate to use equation (6) were the proper values for the fractions of DEL: $P_1$, $P_2$, $P_3$, and $P_4$. Due to the image points being at a distance of one DEL, $P_1$ and $P_3$ equaled




Different cases for assignment of coordinates used for approximation of slope.

Fig. 30

1.0. $P_2$ and $P_4$ were calculated by the distance formula between any two points in a plane.

$$P_2 = \left( (x_2 - x_3)^2 + (y_2 - y_3)^2 \right)^{\frac{1}{2}} / \text{DEL}$$

$$P_4 = \left( (x_1 - x_2)^2 + (y_1 - y_2)^2 \right)^{\frac{1}{2}} / \text{DEL}$$

Using the appropriately calculated values equation (6) was applied to the edge, and the change in tempreature over one time interval was calculated for those points.

```
C
C
C
C
C
C
C     THIS PROGRAM IS DESIGNED FOR THE STUDY OF HEAT FLOW IN
C     A WHISKER OF A SHAPE DESCRIBED BY THE FUNCTION;
C                 Y=ELL-(A*X**2)/(R**2-X**2)
C     WHERE ...
C         A=A PARAMETER WHOSE VALUE IS PROPORTIONAL
C             TO THE DEGREE OF CURVATURE
C         ELL=LENGTH OF THE WHISKER
C         R=RADIUS OF THE WHISKER
C
C
C     ***********************************************************
C
C     DATA CARD ONE CONTAINS THE FOLLOWING INFORMATION TO BE
C     ENTERED IN A FORMAT(3I5,11F10.5,1I5) IN THE FOLLOWING
C     ORDER:
C
C         N=THE NUMBER OF GRID ELEMENTS IN THE X DIRECTION.
C         M=THE NUMBER OF GRID ELEMENTS IN THE Y DIRECTION.
C         INTER8=THE NUMBER OF ITERATIONS DESIRED BETWEEN
C                PRINTOUTS OF THE TEMPERATURE ARRAY.
C         ELL=LENGTH OF THE WHISKER.
C         TSURF=INITIAL SURFACE TEMPERATURE.
C         TINT=TEMPERATURE OF THE BASE AND ATMOSPHERE.
C         DEL=SIZE OF THE UNIT GRID.
C         F=THERMAL CONDUCTIVITY OF THE WHISKER MATERIAL
C           DIVIDED BY ITS HEAT CAPACITY
C         RHO=DENSITY OF THE WHISKER MATERIAL.
C         TIMINT=TIME REPRESENTED BY ONE ITERATION.
C         SIGMA=A PARAMETER USED TO INDICATE THE FLUX
C               THROUGH THE BOUNDARY.
C         FINCR=A CONSTANT REPRESENTING THE TEMPERATURE
C               CHANGE DUE TO CHEMICAL REACTION PER
C               ITERATION
C         IDCID=A NUMBER USED TO EXERCISE THE CONTOUR OPTION
C               1=USE OF OPTION TO CONTOUR TEMPERATURES.
C               0=DESIRE NOT TO CONTOUR.
C
C     ***********************************************************
C
C     DATA CARD TWO CONTAINS A NUMBER CALLED TAU IN A
C     FORMAT(1F10.5). THIS VALUE IS USED TO LABEL THE
C     PRINTOUT INDICATING THE NUMBER OF ITERATIONS
C     PERFORMED UP TO THAT TIME. THE PROGRAM WILL TERMINATE
C     WHEN IT NO LONGER HAS A TAU TO READ.
C
C     ***********************************************************
C
C     DATA CARDS THREE AND FOUR CONTAIN THE TITLE FOR THE
C     GRAPHS IF THE ARRAY IS CONTOURED. DO NOT INSERT THESE
C     CARDS IF THE CONTOUR OPTION IS NOT EXERCISED.
C
C     ***********************************************************
C
C     THE PROGRAM USED TO CONTOUR THE TEMPERATURE ARRAY IS
C     CALLED CONTUR AND IS CONTAINED IN THE REFERENCE
C     LIBRARY OF THE NAVAL POSTGRADUATE COMPUTER CENTER.
C
C
C
C
C     ***********************************************************
C
C
C
C
C
C
```

```
C
C     THE FOLLOWING ARRAYS ARE DIMENSIONED SUCH THAT FOR
C     AN ELEMENT (I,J), THE MAXIMUM I IS AT LEAST N+2 AND
C     THE MAXIMUM J IS AT LEAST M+2
      REAL*4 T(20,50),P3(50),P4(20),DELTAT(20,50),TXX(50,20)
      INTEGER*2 IN(20,50)
C     THESE ARRAYS DEAL WITH CONTUR
      LOGICAL*1  LTG(3)
      REAL*4  CL(6)
      REAL*8 TITLE(12)
      EQUIVALENCE(TXX,DELTAT)
    1 READ(5,100)N,M,INTER8,ELL,R,TSURF,TINT,DEL,F,A,RHO,
     *TIMINT,SIGMA,FINCR,IDCID
  100 FORMAT(3I5,11F5.2,1I5)
  105 READ(5,110) TAU
  110 FORMAT  (1F10.5)
      N1=N+1
      M1=M+1
      M2=M1+1
      WRITE(6,115)
  115 FORMAT(1H1,T4,'N',T9,'M',T13,'INTER8',T25,'ELL',T35,
     *'R',T40,'TSURF',T52,'TINT',T61,'TIMINT',T73,'DEL',T79,
     *'SIGMA',T90,'FINCR',T100,'TAU',/)
  117 WRITE(6,120)N,M,INTER8,ELL,R,TSURF,TINT,TIMINT,DEL,
     *SIGMA,FINCR,TAU
  120 FORMAT  (1X,3I5,11F10.5,/)
C
C     ******************************************************
C
C     ASSIGN INITIAL TEMPERATURES
C
C     ******************************************************
C
      CALL ASSIGN(N,M,T,ELL,R,TSURF,TINT,DEL,XPX,YPY,P4,P3,
     *IN,A)
C     THE FOLLOWING DO LOOP WRITES THE ARRAY AS PICTURED
C     WITH THE BASE AT THE BOTTOM OF THE PAGE
      NCOUNT=-1
  121 NCOUNT=NCOUNT+1
      J=M1-NCOUNT
      WRITE  (6,130)(T(I,J),I=1,N1)
  130 FORMAT('0',2X18F6.1)
      IF(NCOUNT.EQ.M) GO TO 122
  123 GO TO 121
  122 WRITE  (6,135)
  135 FORMAT(1H1,T4,'THE  IN(I,J)  ARRAY  IS',/)
      NCOUNT=-1
  124 NCOUNT=NCOUNT+1
      J=M1-NCOUNT
      WRITE  (6,140)  (IN(I,J),I=1,N1)
  140 FORMAT(/18I6)
      IF(NCOUNT.EQ.M) GO TO 202
      GO TO 124
C
C     ******************************************************
C
C     ITERATE THE T(I,J) ARRAY THE SPECIFIED NUMBER OF TIMES
C
C     ******************************************************
C
  700 DO 136  I=1,INTER8
  900 CALL TNEW(N,M,DEL,TINT,TSURF,T,IN,DELTAT,P4,P3,TIMINT,
     *F,C,RHO,ELL,R,SIGMA,FINCR)
  136 CONTINUE
      WRITE(6,115)
      WRITE(6,120)N,M,INTER8,ELL,R,TSURF,TINT,TIMINT,DEL,
     *SIGMA,FINCR,TAU
      NCOUNT=-1
  126 NCOUNT=NCOUNT+1
      J=M1-NCOUNT
      WRITE  (6,130)(T(I,J),I=1,N1)
      IF(NCOUNT.EQ.M) GO TO 125
```

```
  127 GO TO 126
  125 READ (5,110) TAU
  202 IF(IDCID.EQ.0) GO TO 700
C
C     ****************************************************
C
C     CONTOUR THE ARRAY OF TEMPERATURES
C
C     ****************************************************
C
  600 READ(5,50) TITLE
   50 FORMAT(6A8)
C     THIS DO LOOP EXTENDS THE SURFACE TEMPERATURES
C     OUT INTO THE ATMOSPHERE FOR A NEATER GRAPH
  141 DO 145 J=1,M1
      DO 144 I=1,N1
      IF(IN(I,J).EQ.1) GO TO 144
  142 IF(IN(I,J).NE.2) GO TO 143
  190 TSAVE=T(I,J)
      GO TO 144
  143 T(I,J)=TSAVE
  144 CONTINUE
  145 CONTINUE
C     THIS DO LOOP ROTATES THE T(I,J) ARRAY ON ITS SIDE
C     MAKING THE RESULTING PLOT EASIER TO UNDERSTAND
  950 DO 10 I=1,N1
      DO 10 J=1,M1
      L=M2-J
   10 TXX(L,I)=T(I,J)
C     THESE VALUES ARE USED BY CONTUR
      LTG(1)=.TRUE.
  146 LTG(2)=.FALSE.
      LTG(3)=.FALSE.
      MX=50
      NL=-6
      IW=5
      IH=7
C     INSERT THE CALL CARD AS SHOWN IN THIS SAMPLE
C     CALL CONTUR(TXX,M1,N1,MX,CL,NL,TITLE,IW,IH,LTG)
  150 GO TO 700
      END


      SUBROUTINE ASSIGN(N,M,T,ELL,R,TSURF,TINT,DEL,XPX,YPY,
     *P4,P3,IN,A)
      REAL*4 T(20,50),P3(50),P4(20),DELTAT(20,50)
      INTEGER*2 IN(20,50)
      RS=R*R
      M1=M+1
      N1=N+1
      M2=M+2
      N2=N+2
C
C     ****************************************************
C
C     INITIALIZE ALL T(I,J) AND IN(I,J)
C
C     ****************************************************
C
      DO 110 J=1,M1
      DO 100 I=1,N1
      IN(I,J)=0
      T(I,J)=TSURF
  100 CONTINUE
  110 CONTINUE
C
C     ****************************************************
C
C     TEST PROXIMITY TO SURFACE AND ASSIGN P3,P4,IN
C
C     ******************************-*********************
C
```

```
      DO 1000 J=1,M1
      Y=(J-1)*DEL
      XP=SQRT((ELL-Y)*RS/(A+ELL-Y))
      DO 900 I=1,N1
      X=(I-1)*DEL
      XPX=XP-X
      IF(XPX.LE.DEL) GO TO 500
      IN(I,J)=1
      GO TO 560
  500 IF(XPX.GT.0.0) GO TO 512
  501 IF (XPX.EQ.0.0) GO TO 515
      IF (J.EQ.1) GO TO 860
  510 GO TO 900
  512 IN(I,J)=1
      IN(I+1,J)=2
      P3(J)=XPX/DEL
      IF (J.EQ.1) GO TO 860
  513 GO TO 560
  515 IN(I,J)=2
      GO TO 1000
  560 YPY=ELL-A*X**2/(RS-X**2)-Y
      IF (YPY.GE.DEL) GO TO 850
      IN(I+1,J+1)=2
      P4(I)=YPY/DEL
  850 DIST=XPX*YPY/SQRT(XPX**2+YPY**2)
  852 P4(1)=1.0
      IF (J.EQ.1) GO TO 860
  853 T(I,J)=TINT*(1.0-EXP(-10.0*DIST*DIST))
      GO TO 900
  860 T(I,J)=TINT
  900 CONTINUE
 1000 CONTINUE
      RETURN
      END

      SUBROUTINE TNEW(N,M,DEL,TINT,TSURF,T,IN,DELTAT,P4,P3,
     *TIMINT,F,C,RHO,ELL,R,SIGMA,FINCR)
      REAL*4 T(20,50),P3(50),P4(20),DELTAT(20,50)
      INTEGER*2 IN(20,50)
      M1=M+1
      N1=N+1
C
C     *******************************-***********************
C
C     SET UP THE TEMPERATURES TO BE USED IN THE MOLECULE
C
C     *******************************************************
C
C     IF THE TEMPERATURE IS ON THE EDGE CALL TEDGE OTHERWISE
C     CALL DERIV
    5 DO 1000 J=1,M1
   10 DO 900 I=1,N1
      IF (IN(I,J).EQ.2) GO TO 850
   11 IF (IN(I,J).EQ.0) GO TO 860
   12 Z0=T(I,J)
      IF (I.EQ.1) GO TO 15
      Z1=T(I-1,J)
      GO TO 20
   15 Z1=T(I+1,J)
   20 IF (J.EQ.1) GO TO 25
      Z2=T(I,J-1)
      GO TO 30
   25 Z2=TINT
   30 IF (IN(I,J+1).EQ.2) GO TO 50
      Z4=T(I,J+1)
      GO TO 60
   50 Z4=T(I+1,J+1)
   60 Z3=T(I+1,J)
      IF(J.NE.M) GO TO 70
   62 IF(I.EQ.1) GO TO 65
   63 Z4=T(I+1,J+1)
```

```
      GO TO 70
   65 Z4=T(I,J+1)
   70 CALL DERIV (Z0,Z1,Z2,Z3,Z4,ELL,R,DEL,TIMINT,IN,F,
     *C,RHO,P4,P3,DELTAT,I,J,N,A,T,SIGMA)
  840 GO TO 900
  850 CALL TEDGE(IN,DELTAT,P3,P4,DEL,I,J,T,R,TIMINT,M,F,C,
     *RHO,FINCR,TINT,SIGMA)
C     KEEP THE BASE AT CONSTANT TEMPERATURE
      GO TO 900
  860 DELTAT(I,J)=0.0
  900 CONTINUE
 1000 CONTINUE
C
C     *****************************************************
C
C     INTERPOLATE TO FIND CHANGE AT POINTS WHERE
C     BOUNDARY CROSSES Y GRID LINE
C
C     *****************************************************
C
      DO 2000 J=1,M
      DO 1900 I=2,N1
      IF(IN(I,J).EQ.0) GO TO 2000
 1700 IF(IN(I-1,J).NE.2) GO TO 1900
 1800 DELTAT(I,J)=DELTAT(I,J-1)+P4(I-1)*(DELTAT(I-1,J)-
     *DELTAT(I,J-1))
      GO TO 2000
 1900 CONTINUE
 2000 CONTINUE
C
C     *****************************************************
C
C     CALCULATE THE NEW TEMPERATURE
C
C     *****************************************************
C
      DO 1010 J=1,M1
      DO 1009 I=1,N1
 1008 T(I,J)=T(I,J)+DELTAT(I,J)
 1009 CONTINUE
 1010 CONTINUE
 1020 CONTINUE
      RETURN
      END


      SUBROUTINE DERIV (Z0,Z1,Z2,Z3,Z4,ELL,R,DEL,TIMINT,IN,
     *F,C,RHO,P4,P3,DELTAT,I,J,N,A,T,SIGMA)
      REAL*4 T(20,50),P3(50),P4(20),DELTAT(20,50)
      INTEGER*2 IN(20,50)
C
C
C     *****************************************************
C
C     CALCULATE THE TEMPERATURE DIFFERENCE OVER THE TIME
C     INTERVAL
C
C     *****************************************************
C
      IF(J.EQ.1) GO TO 95
   10 N1=N+1
      Y=(J-1)*DEL
      X=(I-1)*DEL
      IF(IN(I+1,J).EQ.2) GO TO 40
   35 PP3=1.0
      GO TO 50
   40 PP3=P3(J)
   50 IF(IN(I,J+1).EQ.2) GO TO 60
   55 PP4=1.0
      GO TO 70
   60 PP4=P4(I)
   70 ALPHA=F/(C*RHO)
```

```
      IF (X.GT.0.0) GO TO 80
   75 X=DEL
   80 S1=(2.0/(DEL*DEL))*(Z3/(PP3*(PP3+1.0))-Z0/PP3+
     *Z1/(PP3+1.0)+Z4/(PP4*(PP4+1.0))-Z0/PP4+Z2/(PP4+1.0))
      S2=(1.0/(X*DEL*(PP3+1.0)))*(Z3/PP3-PP3*Z1-Z0/PP3+PP3*Z
   89 ALPHA=F/RHO
   90 DELTAT(I,J)=ALPHA*(S1+S2)*TIMINT
      GO TO 120
   95 DELTAT(I,J)=0.0
  120 RETURN
      END


      SUBROUTINE TEDGE(IN,DELTAT,P3,P4,DEL,I,J,T,R,TIMINT,M,
     *F,C,RHO,FINCR,TINT,SIGMA)
      REAL*4 T(20,50),P3(50),P4(20),DELTAT(20,50)
      INTEGER*2 IN(20,50)
      M1=M+1
      IF(J.EQ.1) GO TO 900
C     FIND THE X AND Y COORDINATES OF THE POINT
   80 IF(I.EQ.1) GO TO 550
   40 IF(IN(I-1,J).NE.2) GO TO 50
      X=(I-2)*DEL
      Y=(J-2+P4(I-1))*DEL
   45 GO TO 110
   50 IF(J.NE.M1) GO TO 100
   70 X=(I-2)*DEL
      Y=(J-2+P4(I-1))*DEL
   90 GO TO 110
  100 X=(I-2+P3(J))*DEL
      Y=(J-1)*DEL
C
C     ****************************************************************
C
C     CALCULATE THE X AND Y COORDINATES OF THE EDGE POINTS
C     ON EITHER SIDE OF THE POINT UNDER CONSIDERATION
C
C     ****************************************************************
C
  110 X2=X
      Y3=(J-2)*DEL
      X3=(I-2+P3(J-1))*DEL
      IF(J.NE.M1) GO TO 106
      Y2=(J-2+P4(I-1))*DEL
      X3=(I-1)*DEL
      Y1=(J-2+P3(I-2))*DEL
      X1=(I-3)*DEL
      IF(IN(I,J-1).EQ.2) GO TO 105
  104 Y3=(J-2+P4(I))*DEL
      GO TO 125
  105 Y3=(J-2)*DEL
      X3=(I-2+P3(J-1))*DEL
      GO TO 125
  106 IF(IN(I-1,J).EQ.2) GO TO 120
  112 IF(IN(I+1,J).EQ.2) GO TO 121
  111 IF(IN(I-1,J+1).EQ.2) GO TO 116
  115 X1=(I-2+P3(J+1))*DEL
      Y1=(J*DEL)
      Y2=(J-1)*DEL
      GO TO 125
  116 X1=(I-2)*DEL
      Y1=(J-1+P4(I-1))*DEL
      Y2=(J-1)*DEL
      GO TO 125
  120 X1=(I-3+P3(J))*DEL
      Y1=(J-1)*DEL
      Y2=(J-2+P4(I-1))*DEL
      GO TO 125
  121 X3=(I-1)*DEL
      Y3=(J-2+P4(I))*DEL
      Y2=(J-1)*DEL
      IF(IN(I-1,J+1).EQ.2) GO TO 123
```

```
  122 X1=(I-2+P3(J+1))*DEL
      Y1=J*DEL
      GO TO 125
  123 X1=(I-2)*DEL
      Y1=(J-1+P4(I-1))*DEL
C
C     ******************************************************
C
C     CALCULATE THE SLOPE
C
C     ******************************************************
C
  125 X3X2=X3-X2
      X1X2=X1-X2
      V1=Y3-((X3X2*X3X2)/(X1X2*X1X2))*Y1
      V2=Y2-((X3X2*X3X2)/(X1X2*X1X2))*Y2
      V3=X3-X2-(X3X2*X3X2)/(X1X2)
      DYDX=(V1-V2)/V3
C
C     ******************************************************
C
C     FIND THE IMAGE TEMPERATURE
C
C     ******************************************************
C
  130 DY=DEL*(SQRT(1.0/(1.0+DYDX*DYDX)))
      DX=DEL*(SQRT(1.0/(1.0+1.0/(DYDX*DYDX))))
  200 XTERP=(X-DX)-(I-3)*DEL
      XT=XTERP/DEL
  365 IF(J.EQ.M1) GO TO 370
  375 IF(IN(I-1,J).EQ.2) GO TO 310
      YTERP=DEL-DY
  320 GO TO 360
  310 IF(DYDX.GT.-2.10) GO TO 370
  314 YTERP=P4(I-1)*DEL-DY
      GO TO 360
  370 YTERP=(1.0+P4(I-1))*DEL-DY
  360 YT=YTERP/DEL
      IF(IN(I-1,J).NE.1) GO TO 645
  646 GO TO 660
C     IN AREAS OF HIGH CURVATURE A DIFFERENT SET OF POINTS
C     MUST BE USED
  645 IF(DYDX.GT.-2.1) GO TO 606
 601  GO TO 660
  606 T01=T(I-2,J-1)
      T11=T(I-1,J-1)
      T00=T(I-2,J-2)
      T10=T(I-1,J-2)
      T0N1=T(I-2,J-3)
      IF(I.LE.3) GO TO 650
  605 TN10=T(I-3,J-2)
      GO TO 700
  650 TN10=T(I-1,J-2)
      GO TO 700
  660 T00=T(I-2,J-1)
      T10=T(I-1,J-1)
      T01=T(I-2,J)
      TN10=T(I-3,J-1)
      T11=T(I-1,J)
      IF(J.EQ.2) GO TO 690
  640 T0N1=T(I-2,J-2)
      GO TO 700
  690 T0N1=TINT
  700 W1=T00*(1.0-XT*XT-YT*YT+XT*YT)
      W2=T10*(0.5*XT+0.5*XT*XT-XT*YT)
      W3=TN10*(-0.5*XT+0.5*XT*XT)
      W4=T01*(0.5*YT+0.5*YT*YT-XT*YT)
      W5=T0N1*(-0.5*YT+0.5*YT*YT)
      W6=T11*(XT*YT)
      TIMAGE=W1+W2+W3+W4+W5+W6
C     SET UP THE EDGE MOLECULES
  203 Z0=T(I,J)
```

```
      TIMAG2=TIMAGE-2.0*DEL*SIGMA*(TINT-T(I,J))
      Z1=TIMAGE
      Z2=T(I,J-1)
      Z3=TIMAG2
  204 Z4=T(I,J+1)
      PP1=1.0
      PP3=1.0
  210 PP2=(SQRT((X2-X3)*(X2-X3)+(Y2-Y3)*(Y2-Y3)))/DEL
  211 PP4=(SQRT((X1-X2)*(X1-X2)+(Y1-Y2)*(Y1-Y2)))/DEL
      IF(J.NE.M1) GO TO 240
      TIMAG2=TIMAGE-2.0*DEL*SIGMA*(TINT-T(I,J))
  241 Z0=T(I,J)
      Z1=TIMAGE
      Z3=TIMAG2
      IF(IN(I-1,J).NE.0) GO TO 349
  345 Z4=T(I-2,J)
      GO TO 350
  349 Z4=T(I-1,J)
  350 IF(IN(I,J-1).EQ.2) GO TO 207
      Z2=T(I+1,J)
      GO TO 208
  207 Z2=T(I,J-1)
  208 PP1=1.0
      PP3=1.0
      PP2=1.0
      PP4=1.0
  240 IF(IN(I-1,J).EQ.2) GO TO 525
  300 IF(IN(I+1,J).EQ.2) GO TO 500
  302 GO TO 600
  500 Z2=T(I+1,J)
      GO TO 600
  525 Z4=T(I-1,J)
      GO TO 600
  550 Z0=T(I,J)
      Z1=T(I+2,J)
      Z3=Z1
      Z2=T(I,J-1)
      TIMAG2=TIMAGE-2.0*DEL*SIGMA*(TINT-T(I,J))
      Z4=TIMAG2
      X=1.0
  590 PP1=1.0
      PP2=PP1
      PP3=PP1
      PP4=PP1
  600 S1=(2.0/(DEL*DEL))*((1.0/(PP3*PP3+PP3*PP1))*(Z3-Z0*(1.
     *+PP3*Z1/PP1))
      S2=(2.0/(DEL*DEL))*((1.0/(PP4*PP4+PP4*PP2))*(Z4-Z0*(1.
     *+PP4*Z2/PP2))
      S3=-FINCR
      ALPHA=F/RHO
  800 DELTAT(I,J)=ALPHA*(S1+S2)*TIMINT+S3
      GO TO 1000
  900 DELTAT(I,J)=0.0
 1000 RETURN
      END
```

BIBLIOGRAPHY


1. Levitt, A. P., ed., Whisker Technology, Wily-Interscience, 1970, p. 60.

2. Brenner, S. S., "Factors Influencing the Strength of Whiskers," Fiber Composite Materials, American Society for Metals, 1965, p. 11

3. Frank, F. C., "The Inluence of Dislocations on Crystal Growth," Discussions of the Faraday Society, no. 5, 1949, p. 48.

4. Burton, W. K., Cabrera, N., and Frank, W. C., "The Growth of of Crystals and the Equilibrium Structure of Their Surfaces," Philisophical Transactions of the Royal Society, v. 203A, p. 299.

5. Brenner, S. S., "The Growth of Whiskers by the Reduction of Metal Salts, "Acta Metallurgica, v. 4, January 1956, p. 62.

6. Kittaka, S. and Kaneko, F., " Growth of a Large Number of Iron Whiskers by the Reduction of Halides, "Japanese Journal of Applied Physics, v. 8, no. 7, July 1969, p. 860.

7. Kittaka, S. and Kiyoshi, K., "Growth of Copper Whiskers from Dupric Oxide," Japanese Journal of Applied Physics, v. 8, September 1965, p. 661.

8. Melmed, A. J. and Gomer, R., "Field Emission from Whiskers," The Journal of Chemical Physics, v. 34, no. 5, May 1960, p. 1802.

9. Faktor, M. M., Garrett, I., and Heckingbottom, R., "Diffusion Limitations in Gas Phase Growth of Crystals, " Journal of Crystal Growth, v. 9, 1971, p. 3.

10. Faktor, M.M., Garrett, I., "Interplay of Activation and Diffusion in Crystal Growth from the Vapor Phase," Journal of Crystal Growth, v. 9, 1971, p. 3.

11. Holman, J. P., Heat Transfer, 3rd ed., McGraw-Hill Book Company, New York, 1972.

12. Chao, T. T., ed., Advanced Heat Transfer, Clausing, A. M. "Numerical Methods in Heat Transfer," University of Illinois Press, 1969, p. 157.

13. Wylie, D. R., Jr., Advanced Engineering Mathematics, McGraw-Hill Book Company, Inc., 1951, p. 590.

14. Mickley, H. S., Sherwood, T. K., and Reed, E. E., Applied Mathematics in Chemical Engineering, McGraw-Hill, 1957, p. 373.

15. Buckley, H. E., Crystal Growth, John Wiley and Sons, Inc., 1951, p. 488.

16. Wicks, C. E., and Block, F. E., Bulletin 605 Bureau of Mines, Thermodynamic Properties of 65 Elements - Their Oxides, Halides, Carbides, and Nitrides, United States Government Printing Office, Washington, 1963.

17. Lapidus, L., Digital Computation for Chemical Engineers, McGraw-Hill Book Company, Inc., 1962.

18. St. Pierre, G. R., ed., Physical Chemistry of Process Metallurgy - Part 2, Metallurigical Society Conferences, v. 8, Interscience Publishers, 1959, p. 771.

19. Duckley, H. E., Crystal Growth, John Wiley and Sons, Inc., 1951.

20. Doremus, R. H., Roberts, B. W., Trumball, D., Growth and Perfection of Crystals, John Wiley and Sons, Inc., 1958.

INITIAL DISTRIBUTION LIST

| | | No. Copies |
|---|---|---|
| 1. | Defense Documentation Center<br>Cameron Station<br>Alexandria, Virginia 22314 | 2 |
| 2. | Library, Code 0212<br>Naval Postgraduate School<br>Monterey, California 93940 | 2 |
| 3. | Professor W. M. Tolles, Code 5417<br>Department of Material Science and Chemistry<br>Naval Postgraduate School<br>Monterey, California 93940 | 1 |
| 4. | ENS Mark D. Hovermale, USN<br>Whitacre, Virginia 22662 | 1 |

Security Classification

**DOCUMENT CONTROL DATA - R & D**

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

| | |
|---|---|
| 1. ORIGINATING ACTIVITY *(Corporate author)*<br>Naval Postgraduate School<br>Monterey, California 93940 | 2a. REPORT SECURITY CLASSIFICATION<br>Unclassified<br>2b. GROUP |

3. REPORT TITLE

An Examination of the Cold Tip Theory of Whisker Growth

4. DESCRIPTIVE NOTES *(Type of report and, inclusive dates)*

Master's Thesis; June 1972

5. AUTHOR(S) *(First name, middle initial, last name)*

Mark D. Hovermale

| 6. REPORT DATE | 7a. TOTAL NO. OF PAGES | 7b. NO. OF REFS |
|---|---|---|
| June 1972 | 110 | 20 |

| | |
|---|---|
| 8a. CONTRACT OR GRANT NO.<br>b. PROJECT NO.<br>c.<br>d. | 9a. ORIGINATOR'S REPORT NUMBER(S)<br>9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* |

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited

| 11. SUPPLEMENTARY NOTES | 12. SPONSORING MILITARY ACTIVITY |
|---|---|
| | Naval Postgraduate School<br>Monterey, California 93940 |

13. ABSTRACT


A new consideration in the growth mechanism of whiskers is examined. The heat flow due to the shape of the crystal and the thermodynamics of the growth reaction is believed to be an important factor in the unidirectional growth observed in whiskers. A computer program was formulated to model the heat flow as well as a method to calculate the time necessary for the temperature changes to occur.

It was found that there is substantial reason to believe the whisker tip is significantly cooler than the sides. This phenomenon is referred to as the cold tip mechanism which provides a preferential growth site for reaction at the tip.

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Crystal | | | | | | |
| Whisker | | | | | | |
| Cold tip theory | | | | | | |
| Iron whisker | | | | | | |
| Copper whisker | | | | | | |

Thesis 135636
H8212 Hovermale
c.1 An examination of the cold tip theory of whisker growth.